acidic solution was made strongly alkaline with sodium hydroxide solution and extracted with ether. The extract was dried and evaporated. The residue was distilled in a short-path apparatus giving a mixture shown by ir and glpc to contain *o*-toluidine and triethyl phosphate but no 2-acetylpyridine.

_o_-Azidotoluene. *o*-Azidotoluene was prepared from toluidine (76% yield) by Smolinsky's modification[36] of the general procedure of Smith and Brown.[37]

Photolysis of _o_-Azidotoluene in Triethyl Phosphate. A solution of *o*-azidotoluene (6.65 g, 0.05 mol) in triethyl phosphate (200 ml) was photolyzed for 24 hr with a 450-W Hanovia lamp (Pyrex filter). After this irradiation period, glpc indicated 49% of the azide had been decomposed. The triethyl phosphate and unreacted azide were removed by distillation and the residue was processsed by the hydrolytic work-up procedure (method B). The basic product was identified as toluidine (37 mg). No 2-acetylpyridine was detected.

Photolysis of _o_-Azidotoluene in Diethylamine. A solution of the azide (5.5 g, 0.041 mol) in diethylamine (180 ml) was photolyzed under nitrogen for 40 hr using a 200-W Hanovia lamp (Pyrex filter). The excess diethylamine was removed on a rotary evaporator, and the residue was distilled giving recovered *o*-azidotoluene (0.5 g) and 2-diethylamino-3-methyl-3H-azepine (**10b**) (2.25 g, 0.0126 mol, 31%). The nmr and infrared spectra were identical with the sample prepared by photochemical deoxygenation of *o*-nitrotoluene.

Anal. Calcd for $C_{11}H_{18}N_2$: C, 74.11; H, 10.18; N, 15.71. Found: C, 73.99; H, 10.03 N, 15.82.

Acknowledgment. We thank Mr. Stuart R. Suter and Mrs. C. C. Lang for permission to include certain of their experimental results in this paper.

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(36) G. Smolinsky, *J. Org. Chem.*, **26**, 4108 (1961).

(37) P. A. S. Smith and B. B. Brown, *J. Am. Chem. Soc.*, **73**, 2438 (1951).

The Oxidation of 2-Propanol by Bromine and by Hypobromous Acid in Aqueous Solution

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Contribution from the Department of Physical Chemistry, Hebrew University, Jerusalem, Israel, and the Institute of Chemistry, Tel Aviv University, Tel Aviv, Israel. *Received March 11, 1968*

Abstract: The rate of oxidation of 2-propanol by bromine water at pH 6.7 is confirmed[2] to be higher than in acid solution. However, the dependence of the rate on the concentration of added bromide shows that the pH effect cannot be due to hypobromous acid being a faster oxidizing agent than molecular bromine. The *converse* assumption, *viz.*, $k_{\mathrm{HOBr}} \ll k_{\mathrm{Br_2}}$, is shown to be consistent with these results. This is further confirmed by the slowness of the reaction in bromine-free hypobromous acid solution. Tribromide ion is found to be kinetically inactive. On this basis, $k_{\mathrm{Br_2}}$ is calculated and found to increase with pH even more strongly than does the observed rate constant. As in previous cases, it is suggested that this increase of $k_{\mathrm{Br_2}}$ with increasing pH might be due to the anion $\mathrm{RO^-}$ being oxidized at a very much higher rate than the molecule ROH. The correlation between the pK of the substrate and the form of the curve representing the dependence of the rate constant on pH is discussed.

A number of hydroxylic substances are quantitatively oxidized by bromine water,[3-7] no substitution taking place provided the pH is not too high. The rate of the reaction increases with increasing pH in a manner which in some cases parallels the increase in the relative concentration of hypobromous acid with increasing pH, according to

$$\mathrm{Br_2 + H_2O \rightleftharpoons H^+ + Br^- + HOBr} \qquad \text{(I)}$$

The hypothesis that hypobromous acid should be a more rapid oxidizing agent than molecular bromine might therefore seem attractive.[8] However, for formic acid,[4] ethanol[3,6] acetaldehyde hydrate,[3,6] methanol,[9] and D-glucose,[5] where this hypothesis was subjected to closer scrunity, it proved to be untenable. Firstly, the oxidation by bromine-free hypobromous acid was extremely slow.[3-6] Secondly, the increase of the rate with increasing pH was most pronounced when the formation of hypobromous acid was largely *repressed* by the addition of bromide.[6]

Nevertheless, the influence of pH on the rate of oxidation of 2-propanol by bromine has recently been interpreted[2] on the basis of the hypobromous acid hypothesis. Our findings on the pH dependence of the rate of oxidation of ethanol[6] were adduced as a corroboration of this hypothesis, whereas our interpretation of the effect was rejected.[2]

It therefore seemed desirable to take up once more the question of the kinetically active species in bromine

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(1) (a) Hebrew University, Jerusalem, Israel. (b) Tel Aviv University, Tel Aviv, Israel.

(2) N. C. Deno and N. H. Potter, *J. Am. Chem. Soc.*, **89**, 3555 (1967).

(3) L. Farkas, B. Perlmutter, and O. Schächter, *ibid.*, 71, 2829 (1949).

(4) L. Binoun and B. Perlmutter-Hayman, *Bull. Res. Council Israel*, **5A**, 52 (1955), where literature is quoted.

(5) B. Perlmutter-Hayman and A. Persky, *J. Am. Chem. Soc.*, **82**, 276, 3809 (1960).

(6) B. Perlmutter-Hayman and Y. Weissmann, *ibid.*, 84, 2323 (1962).

(7) P. T. McTigue and J. M. Sime, *J. Chem. Soc.*, 1303 (1963); P. T. McTigue, *Australian J. Chem.*, 17, 1210 (1964); J. Konecny, *Helv. Chim. Acta*, **48**, 1817 (1965); see also R. Stewart, "Oxidation Mechanisms," W. A. Benjamin, Inc., New York, N. Y., 1964, p 131.

(8) K. C. Grover and R. C. Mehrota, *Z. Physik. Chem.* (Frankfurt), **14**, 345 (1958).

(9) B. Perlmutter, unpublished results, 1950.

water. In particular, it seemed worth investigating whether 2-propanol might differ from the substances mentioned above, and be oxidized by hypobromous acid more rapidly than by bromine.

Experimental Section

All experiments were carried out at 25 ± 0.05°. The oxidizing capacity was measured by titration with 0.01 N sodium thiosulfate solution; the initial concentration of oxidizing agent was $a = (4\text{-}6) \times 10^{-3}$ M, and that of the 2-propanol was 0.08–0.10 M. The alcohol was thus in sufficient excess for the reaction to be treated as a pseudo-first-order one.

All the reagents employed were analytical grade; the 2-propanol was Mallinckrodt AR or Eastman Spectral Grade. Duplicate experiments with the alcohols of different provenance gave consistent results.

Hypobromous acid solutions were prepared by mixing yellow mercuric oxide and bromine water and distilling *in vacuo* in an all-glass apparatus.[10] The reaction mixtures were protected from bright light.

Results

a. Oxidation by Bromine in Acid Solution. In order to determine the rate constant in the virtual absence of hypobromous acid, we carried out experiments in the absence of buffer, where the reaction mixture becomes acid owing to the formation of hydrobromic acid. An observed rate constant defined by the relation

$$k_{\text{obsd}} = \frac{1}{[\text{ROH}]}\frac{\mathrm{d}\ln(a-x)}{\mathrm{d}t} \tag{1}$$

(where x is the number of moles liter^{-1} reacted) decreased slightly as the reaction proceeded. We may ascribe this to the fact that bromine combines with the bromide ion which appears during the reaction to form tribromide, which in previous cases has been found[3-6] to act at a much lower rate than bromine. The concentration of free bromine can be expressed to a good approximation by[5]

$$[\text{Br}_2] = (a - x)\frac{a + K_3 - x}{a + K_3 + x} \tag{2}$$

where K_3 is the dissociation constant of the tribromide. Setting up the rate equation on the assumption that only free bromine is kinetically active, and integrating, we get

$$k_{\text{Br}_2}t = \ln\frac{a}{a-x} + \frac{2a}{K_3}\ln\frac{a}{a-x} - \frac{2a + K_3}{K_3}\ln\frac{a + K_3}{a + K_3 - x} \tag{3}$$

where the two last terms are both small, and are of opposite sign, thus constituting a small correction. Assuming $K_3 = 0.056$,[11] we obtained a straight line when the right side of eq 3 was plotted against time, with

$$k_{\text{Br}_2} = (5.44 \pm 0.06) \times 10^{-3}\ M^{-1}\ \text{sec}^{-1}$$
$$\text{(maximum deviation)}$$

and

$$k_{\text{Br}_2} = (5.09 \pm 0.07) \times 10^{-3}\ M^{-1}\ \text{sec}^{-1}$$
$$\text{(maximum deviation)}$$

in the presence of 0.3 M KNO_3, and in the absence of added salts, respectively.

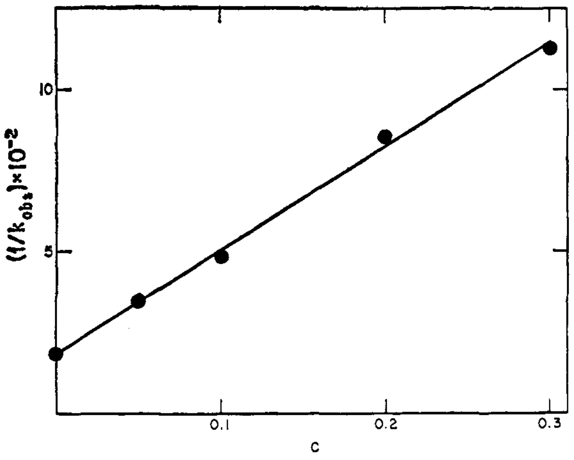

Figure 1. The reciprocal of the observed rate constant, k_{obsd}, as a function of bromide concentration, c.

In order to substantiate our assumption concerning the inactivity of tribromide, we carried out experiments at four different initial bromide concentrations, c, and a total potassium ion concentration of 0.3, kept constant by the addition of KNO_3. Now, provided $(K_3 + c)$ is sufficiently large in comparison with a, the expression

$$[\text{Br}_2] = (a - x)K_3/(K_3 + c) \tag{4}$$

is a good approximation for the concentration of molecular bromine, and if the latter substance is the only oxidizing species, then

$$k_{\text{Br}_2} = k_{\text{obsd}}[1 + (c/K_3)] \tag{5}$$

A slight rearrangement shows that a plot of $1/k_{\text{obsd}}$ *vs.* c should give a straight line, with a slope equal to $1/k_{\text{Br}_2}K_3$. This is illustrated in Figure 1, where we used $k_{\text{Br}_2} = 5.44 \times 10^{-3}$ for k_{obsd} in the total absence of bromide. We obtained $K_3 = 0.057$, in excellent agreement with the value given in the literature.[11]

b. The Reaction at pH 6.7. A pH of 6.7 was achieved by an appropriate mixture of Na_2HPO_4 + KH_2PO_4 (0.3 M in total phosphate). At this pH, both bromine and hypobromous acid are present, their relative concentrations depending on the concentration of added bromide. Conclusions about the rate constants of these two substances can therefore be drawn from the influence of bromide on k_{obsd} at constant pH.

We carried out experiments at five values of c, ranging from $c = 0.04$ where bromine and hypobromous acid are present in approximately equal amounts to $c = 0.30$ where the formation of hypobromous acid is largely repressed. (At the same time, the concentration of the kinetically inactive tribromide increases with increasing values of c). Under these circumstances, the rate equation is

$$\begin{aligned} k_{\text{obsd}} &= (k_{\text{Br}_2}[\text{Br}_2] + k_{\text{HOBr}}[\text{HOBr}])/(a - x) \\ &= k_{\text{Br}_2}\left(\frac{c}{c[1 + (c/K_3)] + K_1/[\text{H}^+]}\right) + \\ &\qquad k_{\text{HOBr}}\left(\frac{K_1/[\text{H}^+]}{c[1 + (c/K_3)] + K_1/[\text{H}^+]}\right) \end{aligned} \tag{6}$$

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[10] Y. Knoller and B. Perlmutter-Hayman, *J. Am. Chem. Soc.*, 77, 3212 (1955).

[11] G. Jones and S. Bäckström, *ibid.*, 56, 1517 (1934).

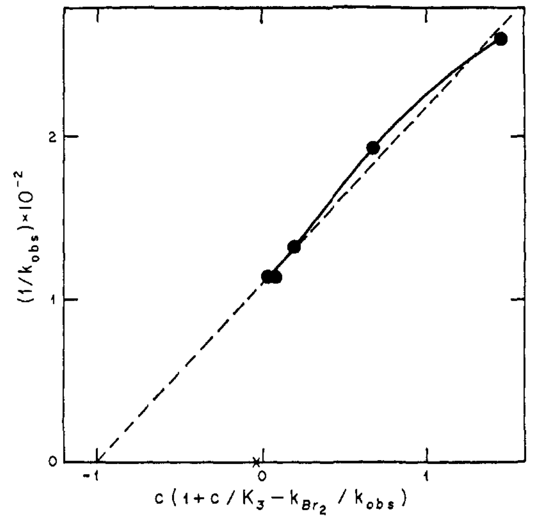

Figure 2. The reciprocal of the observed rate constant, k_{obsd}, against $c[1 + (c/K_3) - (k_{Br_2}/k_{obsd})]$. If the increase in rate with increasing pH is due[2] to the participation of HOBr this should be a straight line passing through $(-K_1/[H^+])$ for $1/k_{obsd} = 0$. The theoretical value of $(-K_1/[H^+])$ is indicated by a cross on the x axis.

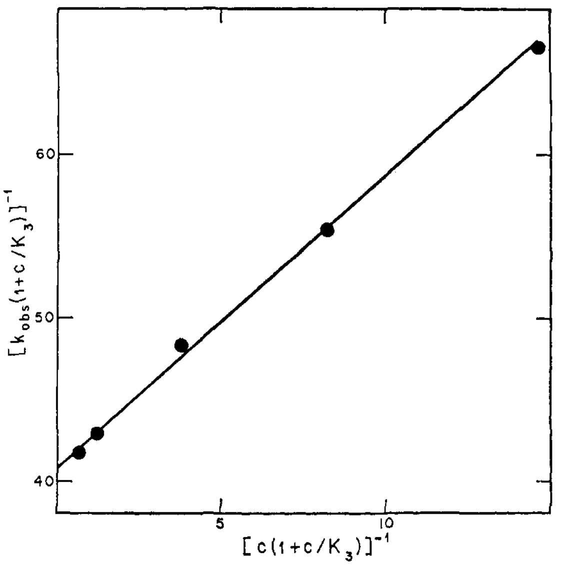

Figure 3. Plot of $\{k_{obsd}[1 + (c/K_3)]\}^{-1}$ *vs.* $\{c[1 + (c/K_3)]\}^{-1}$, where K_3 is the dissociation constant of tribromide. The intercept is the reciprocal of k_{Br_2}; the slope is equal to $K_1/[H^+]k_{Br_2}$, where K_1 is the hydrolysis constant of bromine.

where K_1 is the equilibrium constant of reaction I.

We shall now consider two possibilities. (1) The value of k_{Br_2} remains unaffected by pH, and the increase in k_{obsd} with increasing pH is due to the contribution of hypobromous acid to the observed rate.[2] Equation 6 can then be rewritten in the form

$$c[1 + (c/K_3) - k_{Br_2}/k_{obsd}] = \frac{k_{HOBr}K_1/[H^+]}{k_{obsd}} - K_1/[H^+] \quad (7)$$

Assuming k_{Br_2} and K_3 to be known from our results in section a, we can plot $1/k_{obsd}$ against the left-hand side of eq 7. If assumption 1 is correct, a straight line should be obtained passing through $(-K_1/[H^+])$ for $1/k_{obsd} = 0$. The result is shown in Figure 2. The experimental points are better represented by a curve than a straight line; what is more decisive, no straight line would pass through these points *and* the point $-K_1/[H^+]$ (indicated by a cross on the x axis, where K_1 has been taken from the literature[12,13]). On the other hand, we can draw what seems a reasonable straight line (dashed) through the experimental points *only*. From an extrapolation of this line to $1/k_{obsd} = 0$, we get a value of K_1 which differs from accepted values[12,13] by a factor of about 34. The assumption[2] that $k_{HOBr} > k_{Br_2}$ is therefore not borne out by the $[Br^-]$ dependence of k_{obsd}.

(2) Let us now make the converse assumption, *viz.*, $k_{HOBr} \ll k_{Br_2}$, and neglect the second member in eq 6. We can then write

$$\frac{1}{k_{obsd}[1 + (c/K_3)]} = \frac{K_1/[H^+]}{k_{Br_2}c[1 + (c/K_3)]} + \frac{1}{k_{Br_2}} \quad (8)$$

It will be noted (see eq 5) that $k_{obsd}[1 + (c/K_3)]$ would be the value of k_{Br_2} if the formation of hypobromous acid were totally suppressed. Figure 3 shows a plot of $\{k_{obsd}[1 + (c/K_3)]\}^{-1}$ *vs.* $\{c[1 + (c/K_3)]\}^{-1}$ to be a straight line, as required by eq 8. From the intercept we find

$$k_{Br_2} = 24.5 \times 10^{-3}\ M^{-1}\ \mathrm{sec}^{-1}$$

The value of k_{Br_2} at pH 6.7 is thus again[3-7] considerably higher than in acid solution. From the slope we calculate $(K_1/[H^+]) = 4.4 \times 10^{-2}$. Assuming pH $\sim$ log $[H^+]$, we obtain $K_1 = 8.8 \times 10^{-9}$ at an ionic strength between 0.04 and 0.3, in good agreement with the value[12] of 5.8×10^{-9} at zero ionic strength. This further confirms the assumptions forming the basis of eq 8.

c. The Reaction with Hypobromous Acid. Although the findings of the previous section show that at pH 6.7 the assumption $k_{HOBr} \ll k_{Br_2}$ leads to consistent results, whereas the converse assumption does not, direct experiments with hypobromous acid solution seemed desirable. The dependence of $(a - x)$ on time is shown in Figure 4 for a typical experiment in the absence of buffer or added salts. The reaction is seen to be again[4-7] very slow at the beginning and to gather speed gradually. Since the bromide formed by the reduction of hypobromous acid reacts with the remaining hypobromous acid to liberate an equivalent amount of bromine, the above result can be satisfactorily explained on the assumption that both hypobromous acid and bromine act as oxidizing agents, with $k_{HOBr} \ll k_{Br_2}$.

The rate equation may thus be written in the form

$$\begin{aligned} \mathrm{d}x/\mathrm{d}t &= [k_{HOBr}(a - 2x) + k_{Br_2}x][ROH] \\ &= (k_{Br_2} - 2k_{HOBr})[ROH](x + A) \quad (9) \end{aligned}$$

where

$$A \equiv k_{HOBr}a/(k_{Br_2} - 2k_{HOBr}) \quad (10)$$

We used trial values of A until ln $(x + A)$ *vs.* time gave a straight line. From the results of three experiments we estimate

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(12) H. A. Liebhafsky, *J. Am. Chem. Soc.*, **56**, 1500 (1934).
(13) N. C. Deno and R. E. Fruit, *ibid.*, **90**, 3502 (1968).

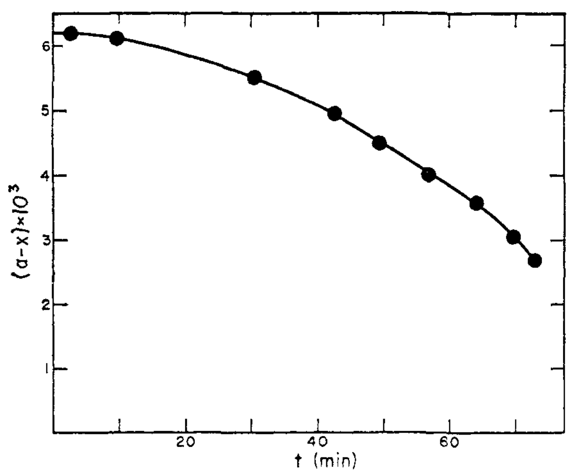

Figure 4. The decrease of $(a - x)$, the concentration of oxidizing substance, with time, for a typical experiment with hypobromous acid, in the absence of buffer.

$$k_{\mathrm{HOBr}} = (0.30 \pm 0.06) \times 10^{-3}\ M^{-1}\ \mathrm{sec}^{-1}$$

$$\text{(maximum deviation)}$$

The large uncertainty in k_{HOBr} stems from the fact that, after a very small percentage of the reaction has taken place, the contribution of the hypobromous acid to the measured rate becomes swamped by that of bromine. Furthermore, eq 9 is based on the assumption that no traces of bromine are either present at the beginning or formed as a result of possible decomposition of hypobromous acid. Our procedure therefore yields only an *upper limit* for k_{HOBr}. It might be added that eq 9 of course holds only while $x \leq a/2$. At larger values of x, no hypobromous acid is left, and the value of $\mathrm{d}\ln(a - x)/\mathrm{d}t$ becomes equal to $k_{\mathrm{Br_2}}/[\mathrm{ROH}]$. This was confirmed by experiment.

At pH 6.7 the reaction with hypobromous acid is even slower to get under way. This is easily understood when we remember that at this pH only a small fraction of the bromide formed will liberate bromine. From the initial rate of reaction we estimate

$$k_{\mathrm{HOBr}} \leq 0.39 \times 10^{-3}\ M^{-1}\ \mathrm{sec}^{-1}$$

From this we calculate that the second member in eq 6 constitutes at most 1.8% of the total rate, and can thus indeed be neglected to a good approximation.

Discussion

Both the influence of bromide concentration on k_{obsd} at pH 6.7 and direct experiments in bromine-free hypobromous acid solution show that $k_{\mathrm{HOBr}} \ll k_{\mathrm{Br_2}}$. On the other hand, not only do we confirm[2] the increase of k_{obsd} with increasing pH,[14] but we calculate a rate constant $k_{\mathrm{Br_2}}$ which increases with increasing pH even more strongly than does k_{obsd}. (This is because in k_{obsd} the pH effect on $k_{\mathrm{Br_2}}$ is partly counteracted by the pH effect on the relative concentrations of HOBr and $\mathrm{Br_2}$.) This increase in $k_{\mathrm{Br_2}}$ with increasing pH is far more pronounced than can be explained by the presence of phosphate, taking into account the general base catalysis recently reported.[7]

Let us now consider the possibility[4–7] that the anion $\mathrm{RO^-}$ should be oxidized at a much higher specific rate than the undissociated molecule ROH. Making use of the fact that at the pH values considered, $[\mathrm{RO^-}] \ll [\mathrm{ROH}]$, we can then write the expression for the observed rate constant

$$k_{\mathrm{obsd}} = (k_{\mathrm{Br_2,ROH}}[\mathrm{Br_2}] + k_{\mathrm{Br_2,RO^-}}[\mathrm{RO^-}]/[\mathrm{ROH}])/(a - x)$$

$$= k_{\mathrm{Br_2,ROH}} \frac{c}{c[1 + (c/K_3)] + K_1/[\mathrm{H^+}]} + k_{\mathrm{Br_2,RO^-}} \frac{K_\mathrm{a}c/[\mathrm{H^+}]}{c[1 + (c/K_3)] + K_1/[\mathrm{H^+}]} \qquad (11)$$

where K_a is the acid dissociation constant of the alcohol. Comparison with eq 6 shows that at a given value of c this assumption leads to the same pH dependence as does the assumption $k_{\mathrm{HOBr}} > k_{\mathrm{Br_2}}$. The latter assumption had been brought forward by Deno and Potter[2] as an explanation of the pH effect. It is only when the dependence on bromide concentration is *also* considered that the two assumptions can be differentiated. It then turns out that the assumption $k_{\mathrm{HOBr}} \ll k_{\mathrm{Br_2}}$ and $k_{\mathrm{Br_2,RO^-}} \gg k_{\mathrm{Br_2,ROH}}$ is compatible with the results, whereas the assumption $k_{\mathrm{HOBr}} > k_{\mathrm{Br_2}}$ is not.

The suggestion that the anion might be oxidized more rapidly than the undissociated molecule has been made before.[4–7] From the data now available, a certain correlation becomes apparent between the pK of the substrate and the pH at which k_{obsd} starts increasing. For formic acid[15] with pK = 3.75 the corresponding pH is below the measurable range.[4] For D-glucose with[16] p$K \sim 12.3$ it is[5] $\sim$1.5; for methanol with[17] p$K \sim 15.5$ it is[9] $\sim$3.5; for ethanol with[17,18] p$K \sim 15.8$ it is $\sim$5. For 2-propanol, which appears to be an even weaker acid than ethanol,[19] the corresponding pH is $\sim$6. This correlation seems to show that the ratio $k_{\mathrm{RO^-}}/k_{\mathrm{ROH}}$ is very roughly the same for all the substances investigated. (Only acetaldehyde with[20] pK = 13.57 and pH of increase[6] $\sim$5 seems to exhibit a substantially lower value for this ratio.) Assuming[5,6] $k_{\mathrm{RO^-}}/k_{\mathrm{ROH}} \sim 5 \times 10^{10}$ we obtain $k_{\mathrm{RO^-}} \sim 2.5 \times 10^{8}$ M^{-1} sec^{-1}, a value which, though well below the diffusion-controlled limit for a second-order reaction, is extremely high for a reaction of this kind. A tentative explanation for the high value of $k_{\mathrm{RO^-}}/k_{\mathrm{ROH}}$ has been given earlier,[5,6] when activation parameters were also discussed.[5]

The rate of oxidation of diisopropyl ether has recently been reported[21] to be independent of pH at low pH, but

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(14) Our values of $k_{\mathrm{obsd}} = 2.08 \times 10^{-3}$ and 7.5×10^{-3}, in acid solution and at pH 6.7, respectively, may be compared with the values of Deno and Potter[2] of 2.59×10^{-3} and 6.70×10^{-3}, at pH 3.85 and 6.65, respectively (all at c 0.1). In view of the probably different concentrations of reactants and added salts, and in view of the sensitivity of k_{obsd} toward small changes in pH at the higher pH, this may be considered reasonable agreement.

(15) H. S. Harned and N. D. Embree, *J. Am. Chem. Soc.*, **56**, 1042 (1934).

(16) Extrapolated from the values given at 0 and 18° by J. Thamsen, *Acta Chem. Scand.*, **6**, 270 (1952).

(17) P. Ballinger and F. A. Long, *J. Am. Chem. Soc.*, **82**, 795 (1960).

(18) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p 68.

(19) J. Hine and M. Hine, *J. Am. Chem. Soc.*, **74**, 5266 (1952).

(20) R. P. Bell and D. P. Onwood, *Trans. Faraday Soc.*, **58**, 1557 (1962).

(21) N. C. Deno and N. H. Potter, *J. Am. Chem. Soc.*, **89**, 3550 (1967).

to decrease rapidly as the pH is increased above 7. The addition of bromide on the one hand decreases the rate of reaction in acid solution, owing to tribromide formation, but on the other hand it shifts the decrease with increasing pH to higher pH values. From these results it is concluded that molecular bromine is a more rapid oxidizing agent for ether than either tribromide or hypobromous acid.[21] All this is very much in line with the present findings. The fact that in this case k_{Br_2} obviously does *not* increase significantly with increasing pH is easily understood when we remember that ethers cannot be expected to form anions. These results thus constitute an indirect confirmation of our suggestion.

It might be added that to our knowledge only oxalic acid and oxalates exhibit a completely different behavior,[10,22] being oxidized by hypobromous acid much more rapidly than by bromine.

Acknowledgment. B. P.-H. wishes to thank Dr. I. Pecht, Max Planck Institut für physikalische Chemie, Göttingen, for helpful discussion during the revision of this paper.

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(22) R. O. Griffith, A. McKeown, and A. G. Winn, *Trans. Faraday Soc.*, 28, 107 (1932); H. A. Liebhafsky and B. Makower, *ibid.*, 29, 597 (1933).

Hydrogenations of Cycloalkenes Using Tris(triphenylphosphine)chlororhodium(I)

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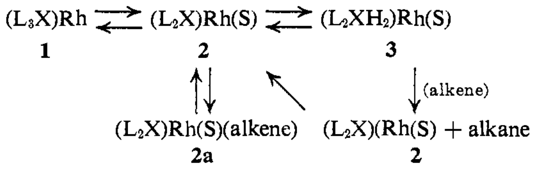
Received August 22, 1968

Abstract: The homogeneous hydrogenations of 1-methylcyclohexene (**4**), 1,4-dimethylcyclohexene (**5**), 1-methyl-4-isopropylcyclohexene (**6**), and 4-methylmethylenecyclohexane (**7**) in benzene and benzene–ethanol solution at 25.0 ± 0.1° under 1 atm of hydrogen using tris(triphenylphosphine)chlororhodium(I) are reported. The three trisubstituted alkenes are hydrogenated very slowly relative to cyclohexene and **7** (15 to 100 times slower). The products formed from **5**, **6**, and **7** are 50.0, 29.9, and 66.6% *cis* isomer, respectively. When deuterium at 1 atm is used, rather extensive exchange is observed in the products from **5** and **6** and the exchange patterns are different in the *cis* and *trans* products while the isomeric products from **7** are very slightly exchanged. The implications of these results relative to the mechanistic details of this reaction are discussed.

The homogeneous catalytic hydrogenation of alkenes using tris(triphenylphosphine)chlororhodium(I) and related complexes as catalysts is currently of considerable interest.[1,2] The most generally satisfactory mechanism is that proposed by Wilkinson[1a] which is summarized in Scheme I. According to this view, the rate-limiting step is the displacement of coordinated solvent (S) from the *cis*-dihydrido species **3** by alkene. The resulting complex is viewed then to progress to product by a fast, *simultaneous* transfer of both hydrogens from the metal atom to the coordinated alkene.[1a] The rate of this reaction is influenced by the nature of the ligand L,[1c,2f] the halogen X,[1a,b] the solvent S,[1a,b] and the alkene[1a,b,2a–d] and conforms to the rate expression[1a]

Scheme I



$$\text{rate} = \frac{k[\mathrm{H_2}][\text{alkene}][\text{catalyst}]}{1 + K_1[\mathrm{H_2}] + K_2[\text{alkene}]}$$

It has been reported that trisubstituted double bonds are not hydrogenated by this procedure.[2a–d] However, it has since been shown that trisubstituted alkenes are indeed hydrogenated under these conditions, albeit very slowly.[1b] We have also found that trisubstituted alkenes undergo hydrogenation using these catalysts and we report here the results of our studies of the hydrogenation and the deuteration of 1-methyl- (**4**), 1,4-dimethyl- (**5**), and 1-methyl-4-isopropylcyclohexene (**6**), and 4-methylmethylenecyclohexane (**7**), using this procedure. The exchange patterns observed when these substrates are reduced in deuterium reveal some very interesting details concerning the several steps of the over-all process.

Results

Initial rates of hydrogenation of the several cycloalkenes were obtained from plots of hydrogen absorption *vs.* time from experiments which were all carried out under the same arbitrary set of experimental conditions in an apparatus we have developed for rate

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