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Radiation Chemistry of Aqueous Solutions of Ethanol and the Nature of the Oxidizing Radical OH[1]

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Nature of the Radical OH

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INTRODUCTION

Czapski and Schwarz (1) have offered proof that the reducing radical formed in water radiolysis, generally referred to as H, bears in fact a negative charge. (It is probably a solvated electron, and is denoted in this paper as H_2O^-.) Their method is based on the effect of added chemically inert salts on the relative reaction rates of the radical with positively and negatively charged ion species. The method depends on the fact that rate constants for reactions between ions of similar charge increase with increasing ionic strength, while rate constants for reactions between ions of opposite charge decrease, and rate constants for reactions between ions and neutral molecules show relatively little change. It seemed worthwhile to apply this method to determine the ionic state of the oxidizing radical formed in water radiolysis, usually called OH.

A system thus had to be found in which the radical will react competitively in neutral water between two solutes bearing different charges. Among the better established reactions in radiation chemistry is the oxidation of ethanol in solutions containing oxygen, originally studied by Jayson, Scholes and Weiss (2) and later used by Schwarz, Caffrey and Scholes (3) to establish the free radical yields in neutral water under irradiation with cyclotron beams. In this system the oxidizing radicals, here denoted as OH, react with the alcohol while the reducing radicals H_2O^- react with oxygen to form a species O_2^- which may be regarded, at least for formalistic purposes, as in equilibrium with its acid form HO_2. The organic radicals formed by attack of OH on the alcohol either add oxygen or react with it to form an aldehyde and HO_2. Two oxygenated radicals then react with one another to form one molecule of peroxide.

$$H_2O \longrightarrow H_2,\ H_2O_2,\ OH,\ H_2O^-$$

$$H_2O^- + O_2 \longrightarrow O_2^- + H_2O \qquad (1)$$

$$O_2^- + H^+ \rightleftarrows HO_2$$

$$OH + C_2H_5OH \longrightarrow H_2O + \cdot C_2H_4OH \qquad (2)$$

$$\cdot C_2H_4OH + O_2 \longrightarrow HO_2 + CH_3CHO$$

$$2HO_2 \longrightarrow H_2O_2 + O_2 \qquad (3)$$

or

$$\cdot C_2H_4OH + O_2 \longrightarrow \cdot O\text{-}O\text{-}C_2H_4OH$$

$$\cdot O\text{-}O\text{-}C_2H_4OH + HO_2 \longrightarrow H_2O_2 + O_2 + CH_3CHO$$

$$2\cdot O\text{-}O\text{-}C_2H_4OH \longrightarrow H_2O_2 + O_2 + 2CH_3CHO$$

From this system we see that each free radical produced from the water leads to formation of one-half molecule of peroxide, to which yield must be added the molecular H_2O_2 formed by recombination of OH radicals in the spurs. The above mechanism thus predicts the observed yields

$$G(H_2O_2) = G_{H_2O_2} + 1/2\ G_{H_2O^-} + 1/2\ G_{OH}$$

$$G(CH_3CHO) = G_{OH}$$

where the parenthesis after the letter G denotes the observed yield of reaction product in molecules per 100 ev, and the G followed by a subscript shows the yields of molecules and radicals produced in radiolysis of water.

In solutions of bromide ion containing oxygen, the reaction mechanism was worked out by Sworski (4) for acid solutions and shown by Allen and Holroyd (5) to apply as well to neutral solutions. Here the H_2O^- reacts with O_2, while the OH reacts with Br^- to form Br atoms which in turn react with peroxide.

$$H_2O^- + O_2 \longrightarrow O_2^- + H_2O \qquad (1)$$

$$O_2^- + H^+ \rightleftarrows HO_2 \qquad ([illegible])$$

$$OH + Br^- \longrightarrow Br + OH^- \qquad (4)$$

$$Br + H_2O_2 \longrightarrow H^+ + Br^- + HO_2 \qquad (5)$$

$$2HO_2 \longrightarrow H_2O_2 + O_2 \qquad (3)$$

Each H atom thus gives rise ultimately to one-half molecule of H_2O_2, while each OH radical destroys one-half molecule, and the peroxide yield predicted from the above mechanism is

$$G(H_2O_2) = G_{H_2O_2} + 1/2\ G_{H_2O^-} - 1/2\ G_{OH}\ .$$

If both bromide and alcohol are present in the solution the above mechanism predicts a yield of peroxide which depends on the ratio of the bromide and alcohol concentrations, since if the OH radical reacts with Br^- it leads to destruction of one-half mole of peroxide while if it reacts with C_2H_5OH it leads to formation of one-half mole of peroxide. The mechanism consisting of equations 1-5 in fact yields the following formula for the observed peroxide yield:

$$G(H_2O_2) = G_{H_2O_2} + 1/2\ G_{H_2O^-} - 1/2\ G_{OH} + \frac{G_{OH}}{1 + k_4(Br^-)/k_2(C_2H_5OH)}$$

In experiments described here the applicability of this formula was verified, the competition constant k_4/k_2 was determined, and the effect of added inert salt on this competition was determined to find out whether the OH radical is really neutral or may exist in some form carrying an electric charge.

EXPERIMENTAL

Triply distilled water, C.P. potassium bromide, C.P. potassium and lithium perchlorate, and absolute alcohol from the Commercial Solvents Corp. were used. In most runs, the solutions were in equilibrium with ordinary air; no acid was present except the normal small amount of carbon dioxide. A few solutions were saturated with oxygen by bubbling with filtered, washed gas. For most of the runs the solutions were irradiated in glass-stoppered test tubes which were cleaned by steaming, followed by pre-irradiation with several megarads while filled with purified water. For hydrogen determinations, the solutions were sealed in tubes, similarly cleaned, and the hydrogen was determined by the method used by Schwarz, Losee and Allen (6). Peroxide was determined by the iodide method of Ghormley (7) and aldehyde by the method of Johnson and Scholes (8). To obtain accurate results by this method it was found necessary to use the purest grade of carbon tetrachloride as a solvent, to store the dinitrophenylhydrazine reagent under refrigeration, and especially to pay close attention to the evolution of optical density with time in both the blank and the unknown solutions. The optical density of the alkaline diphenylhydrazone solution was determined at 430 mμ. The method was calibrated by the use of weighed samples of purified acetaldehyde diphenylhydrazone and the extinction coefficient in the alkaline solution was found to be 16,600 when extrapolated to time of mixing. Two gamma-ray sources were used: one with an intensity of 5.0 krad/min, the other 0.22 krad/min.

RESULTS

The yields of peroxide and aldehyde were found to be entirely independent of radiation intensity. Yields in air-saturated alcohol solutions not containing any bromide are presented in Tables I and II and shown in Fig. 1. At alcohol concentrations of 0.16 m$\underline{M}$ and above the concentrations of aldehyde and peroxide increased linearly with dose and no difficulty was found in obtaining accurate initial G values. At lower concentrations the yield decreased with dose owing no doubt to reaction of OH radicals with the aldehyde and peroxide formed in the reaction, and determination of the initial yields is less certain, but we could find no evidence that the initial yields changed significantly at concentrations of 0.02 or 0.04 m$\underline{M}$. The probable error in the peroxide yields is estimated to be ±0.05 at the higher alcohol concentrations and ±0.1 below 0.1 m$\underline{M}$. The drop in yield at low concentrations reported by Jayson, Scholes and Weiss (2) presumably resulted from their having used too large a dose. At concentrations above 10 m$\underline{M}$ the peroxide yield remains constant but the aldehyde yield increases, in qualitative agreement with their findings.

We suspected this increase might be due to a competition between alcohol and oxygen for the H_2O^- radicals, or H atoms if any of the reducing radicals are produced in this form:

$$H_2O^- + C_2H_5OH = C_2H_4OH\cdot + H_2 + OH^- \qquad (6)$$

This reaction would increase the yield of aldehyde while not affecting the yield of peroxide. To see if this were occurring the hydrogen yield was determined in air-saturated and oxygen-saturated alcohol solutions. The results, which are not very precise owing to the difficulty of determining hydrogen in the presence of a large excess of oxygen and nitrogen gases, are shown in Fig. 2. The data are in qualitative agreement with the postulated competition between alcohol and oxygen for reducing radicals, as the hydrogen yield increases with alcohol concentration, decreases with increasing initial

TABLE I

Initial Yields of Aldehyde in Air-Saturated Ethanol Solutions

(C_2H_5OH), M	G(aldehyde)
4.0×10^{-5}	2.2 ± 0.2
2.06×10^{-4}	2.34 ± 0.1
2.06×10^{-3}	2.34 ± 0.1
2.06×10^{-2}	3.02 ± 0.1
1.20×10^{-1}	3.32 ± 0.1

TABLE II

Initial Peroxide Yields in Air-Saturated Solutions of Ethanol and Potassium Bromide

(C_2H_5OH) mM	(KBr) mM	Added Salt Kind	Added Salt Concn., mM	$G(H_2O_2)$	$G(H_2O_2)_{corr}$
8.9	0	-	-	3.18	3.18
2.2	0	-	-	3.16	3.16
0.22	0	-	-	3.26	3.26
0.18	0	-	-	3.20	3.20
0.18	0	$LiClO_4$	47	3.20	3.20
0.044	0	-	-	3.12	3.12
0.022	0	-	-	3.13	3.13
2.2	2.02	-	-	2.30	2.39
2.2	2.02	$LiClO_4$	50	2.34	2.43
2.2	4.04	-	-	1.83	1.98
2.0	4.04	-	-	1.79	1.94
2.0	4.04	$LiClO_4$	51	1.79	1.94
2.2	6.06	-	-	1.55	1.74
2.2	6.06	$KClO_4$	50	1.57	1.76
0.18	0.202	-	-	2.31	2.36
0.18	0.202	$LiClO_4$	45	2.31	2.36
0.18	0.404	-	-	1.88	1.95
0.16	0.404	-	-	1.86	1.94
0.16	0.404	$LiClO_4$	51	1.86	1.94
0.18	0.606	-	-	1.62	1.71
0.16	0.606	$LiClO_4$	47	1.61	1.70

oxygen concentration and appears to increase further with increasing dose as the oxygen is consumed in the air-saturated runs. The postulated reaction is also consistent with the fact that Jayson, Scholes and Weiss (2) found in oxygen-saturated solutions a less steep rise of aldehyde yield with increasing alcohol concentration than we find in air-saturated solutions. However, the increase in the hydrogen yield in 120 mM alcohol is not great enough to account for the entire increase observed in the initial yield of aldehyde. The rest of the increase in aldehyde yield may arise from reactions occurring in the spurs at high concentrations of alcohol, or possibly from a reaction between alcohol and the radical HO_2. The results of Fig. 2 suggest that k_1/k_6 is of the order of 1500.

The competition between Br^- and alcohol was studied at alcohol concentrations of 2.2 mM and 0.18 or 0.16 mM. The peroxide yields observed are shown in Table II and Fig. 3. It is seen that addition of bromide depresses the peroxide yield as expected from the equation given in the Introduction. The results suggest that OH reacts somewhat more slowly with bromide ion than with alcohol, the ratio of the rates being in the neighborhood of 0.6. It is seen however in Fig. 3 that the peroxide yields depend not only on the ratio of bromide to alcohol but also to a slight degree on the total concentration of the substances. Such an effect was expected since the work of Sworski (4) and of Allen and Holroyd (5) had shown that bromide ion at millimolar concentrations produces significant lowering of the molecular yield of hydrogen peroxide, which is due to scavenging of OH radicals by bromide ion in the spurs. Since alcohol reacts with OH even faster than bromide, it too will contribute to this effect. The result is that in the equation for the peroxide yield the term $G_{H_2O_2}$ will appear to be somewhat smaller and the term G_{OH} somewhat larger at the higher concentrations than at the lower. To determine the competition between bromide and alcohol a correction must be made for the scavenging effect. Exactly how to make this correction depends on what is assumed regarding the reaction of the radicals in the spurs. The correction is small, however, and it turns out that the magnitude of the corrections calculated on various assumptions differ from one another no more than the experimental error in the determinations of the peroxide yield. The corrected values shown in Table II were obtained by assuming that when Br^- or C_2H_5OH reacts with OH in the spur the resulting radicals Br or $\cdot C_2H_4OH$ diffuse out into the solution without further reaction, and that an additional OH radical, which would in the absence of scavenger react with the other OH to form H_2O_2, is also released into the solution. The data of Allen and Holroyd (5) on peroxide yields in neutral air-saturated bromide solutions, when corrected to initial yield values by the method mentioned in the 1958 Geneva paper of Allen and Schwarz (9), give the empirical result $G(H_2O_2) = 1.00 - 1.43(Br^-)^{1/3}$. On the basis of the above assumption, and neglecting the effect of scavenging on the combination of OH with the reducing radicals in the spur, this result may be interpreted as indicating that the molecular peroxide yield is decreased by an amount equal to half the total observed decrease in the peroxide yield or $0.715(Br^-)^{1/3}$, while the effective yield of OH or the equivalent Br radicals is increased by $1.43(Br^-)^{1/3}$. In solutions containing alcohol, since alcohol reacts even faster with OH than does Br^-, the total increase in radical yield should be the sum of the contributions of both species and is then reasonably taken as $1.43((Br^-) + (1/0.6)(C_2H_5OH))^{1/3}$ (hereinafter called W), since the ratio of rates of reaction of OH with bromide and alcohol is 0.6. The yield of peroxide on these assumptions is thus given by

$$G(H_2O_2) = G_{H_2O_2} - W/2 + 1/2\ G_{H_2O^*} - 1/2\ G_{OH} - W/2 + \frac{G_{OH} + W}{1 + .6(Br^-)/(C_2H_5OH)}$$

$$= G_{H_2O_2} + 1/2\ G_{H_2O} - 1/2\ G_{OH} + \frac{G_{OH}}{1 + .6(Br^-)/(C_2H_5OH)} - \frac{W}{1 + (C_2H_5OH)/.6(Br^-)}$$

where the G's with subscripts refer to the values appropriate to pure air-saturated water. The corrected yield, which is the yield that would be obtained for any given ratio of Br^- to alcohol concentrations in the absence of scavenging effects, is

$$G(H_2O_2)_{corr} = G(H_2O_2)_{obs} + \frac{W}{1 + (C_2H_5OH)/.6(Br^-)}$$

These corrected values are given in Table II. It may be seen that on the present assumptions, the peroxide yield in solutions containing alcohol but not bromide should not be affected by scavenging. If the assumed mechanism for the reaction holds, the corrected yields should follow the equation

$$G(H_2O_2)_{corr} = 1.00 + \frac{G_{OH}}{1 + .6(Br^-)/(C_2H_5OH)}$$

since by Holroyd's corrected results,

$$G_{H_2O_2} + 1/2\ G_{H_2O^*} - 1/2\ G_{OH} = 1.00$$

Figure 4 shows a plot of the reciprocal of the quantity $(G(H_2O_2)_{corr} - 1.00)$ which should be a linear function of the concentration ratio. The points lie within experimental error on a line of intercept 1/2.3 (the value expected from the aldehyde yields) and a slope corresponding to a competition constant of 0.6. A different formula, based on the assumption that the radicals Br and C_2H_4OH formed by scavenging in the spur do not escape from the spur but react with another OH, was also tried and found to give corrected peroxide yields practically indistinguishable from the ones here presented. The results thus are entirely consistent with the assumed mechanism involving competition between Br^- and C_2H_5OH for the oxidizing free radical.

Table II and Figs. 3 and 4 show also the peroxide yields obtained in the bromide-alcohol mixtures when an inert salt, lithium or potassium perchlorate, was added in a concentration of 50 m$\underline{M}$. The added salt is seen to have no effect on the peroxide yields within experimental error. This is in strong contrast to the results obtained by Czapski and Schwarz (1) on competition for the reducing radical H_2O^- between NO_2^- and H_2O_2 or between H^+ and H_2O_2. They found that adding as little as 20 m$\underline{M}$ of perchlorate or other inert salt changed these competition constants by as much as 40%, in agreement with the accepted theory of the kinetic salt effect. Thus if the oxidizing radical OH were a charged species, the points of Fig. 3 containing added salt would be displaced along the horizontal axis of the figure by more than 40%. In other words, the observed peroxide yields in the presence of added salt would be equal to those found in its absence for a ratio $(Br^-)/(C_2H_5OH)$ over 40% greater or smaller than that used, which, as may be seen from the curve, would cause a large change in the yield. Since no change is observed it must be concluded that essentially all of the oxidizing radicals are uncharged and presumably actually exist in the form OH.

DISCUSSION

It is surprising that OH radicals react with alcohol even faster than with bromide ions. These reactions are presumably diffusion controlled and the activation energy for the reaction of OH with ethanol must be smaller than the activation energy for diffusion of these radicals in water.

Since the oxidizing radicals formed in water radiolysis are neutral, while the conjugate reducing radicals are negatively charged, a positive ion must be produced simultaneously to obtain charge balance. This is presumably the hydrogen ion, and the radiolysis of water must primarily occur with the production of equal amounts of three species: H_2O^-, OH and H^+. There is evidence that H_2O^- reacts at every encounter with either itself or H^+ to give respectively H_2 molecules or H atoms. Thus one would expect that in the diffusion out of the spur H_2 and atomic H should be formed in comparable amounts. Such a picture agrees with the conclusions of Allan and Scholes (10) that the reducing radicals in water radiolysis include H atoms with a yield of 0.6 together with the larger yield of H_2O^-. It seems inconsistent with the finding of Czapski and Allen (11) that in solution of oxygen and hydrogen peroxide the reducing radicals behave as though they were all H_2O^-.

SUMMARY

Solutions containing ethanol, bromide ion and oxygen have been irradiated with gamma rays. The accepted mechanism for the oxidation of alcohol has been confirmed and the competition for OH between Br^- and C_2H_5OH has been demonstrated. The OH radical reacts somewhat faster with ethanol than with bromide ion. Addition of inert salts had no effect on this competition, which demonstrates that the radical is in fact a neutral species and is best represented by the conventional formula OH.

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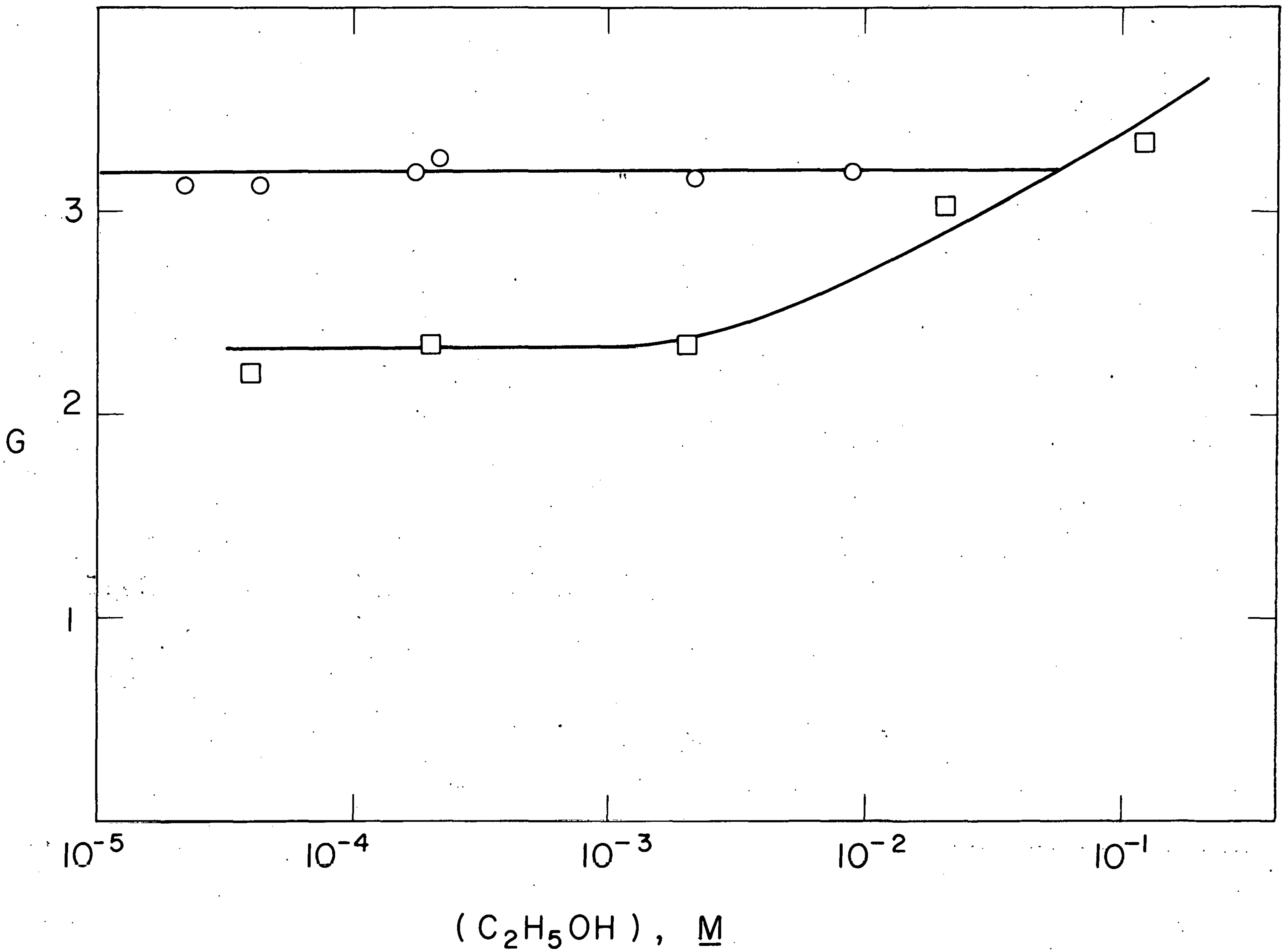
Fig. 1. Yields of peroxide and aldehyde in air-saturated aqueous solutions of ethanol. 0, peroxide; □ , aldehyde.

Fig. 2. Hydrogen concentration vs. dose. 0, 2 mM C_2H_5OH, air-saturated; □ , 120 mM C_2H_5OH, air-saturated; ■ , 120 mM C_2H_5OH, oxygen-saturated.

Fig. 3. Peroxide yields in air-saturated solutions, with and without added $KClO_4$ or $LiClO_4$, vs. concentration ratio of KBr to C_2H_5OH. 0, (C_2H_5OH) near 0.18 mM, no added salt; + , same with 50 mM $LiClO_4$ added; □ , (C_2H_5OH) near 2.2 mM; x , same with 50 mM $LiClO_4$ or $KClO_4$ added.

Fig. 4. $(G(H_2O_2)_{corr} - 1.0)^{-1}$ vs. concentration ratio of KBr to C_2H_5OH. The line corresponds to $k_{OH,Br^-}/k_{OH,C_2H_5OH} = 0.6$.


G
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10^{-5}
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(C_2H_5OH), M

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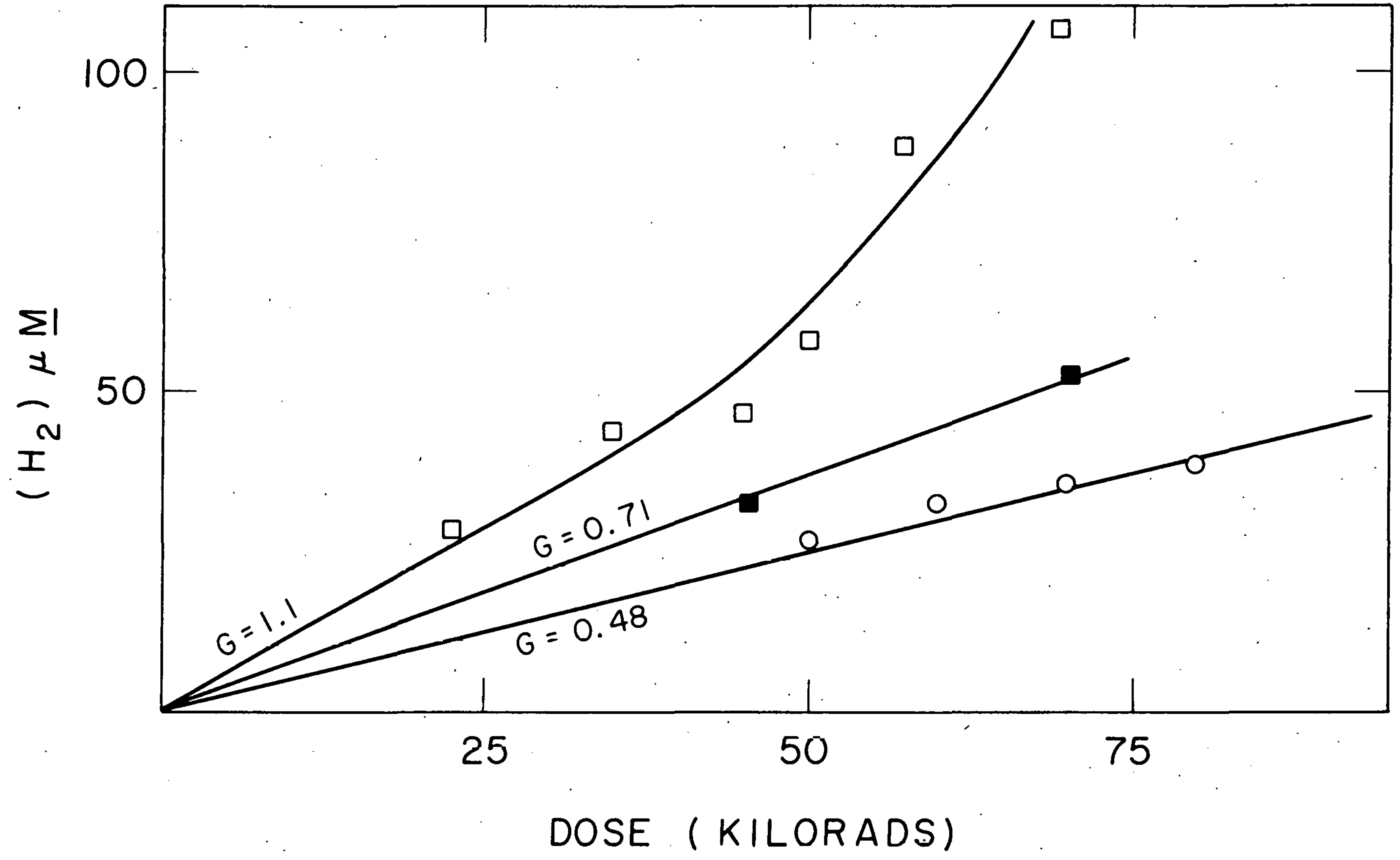

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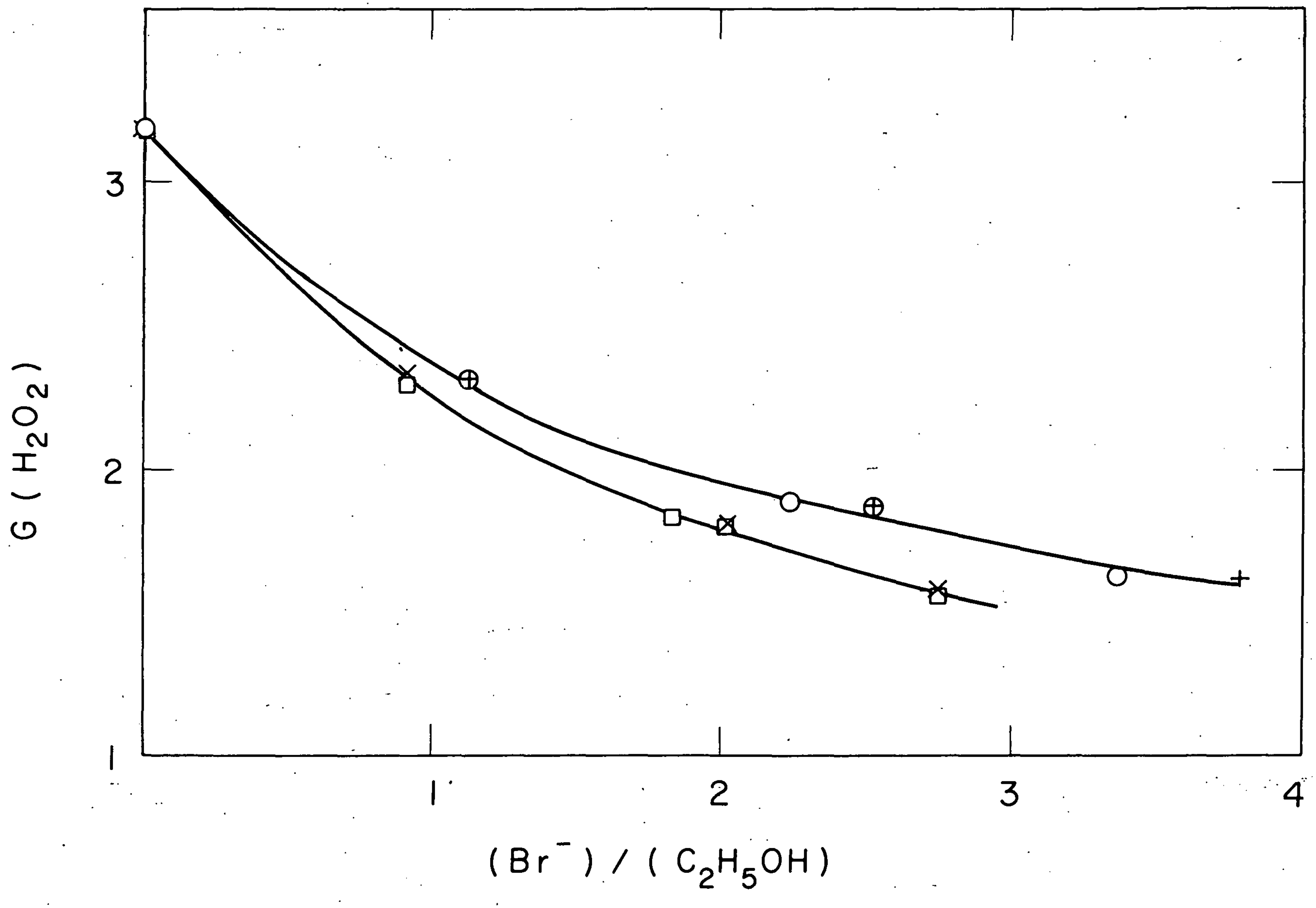
50
(H$_2$) μM
25
50
75
DOSE (KILORADS)
G = 1.1
G = 0.71
G = 0.48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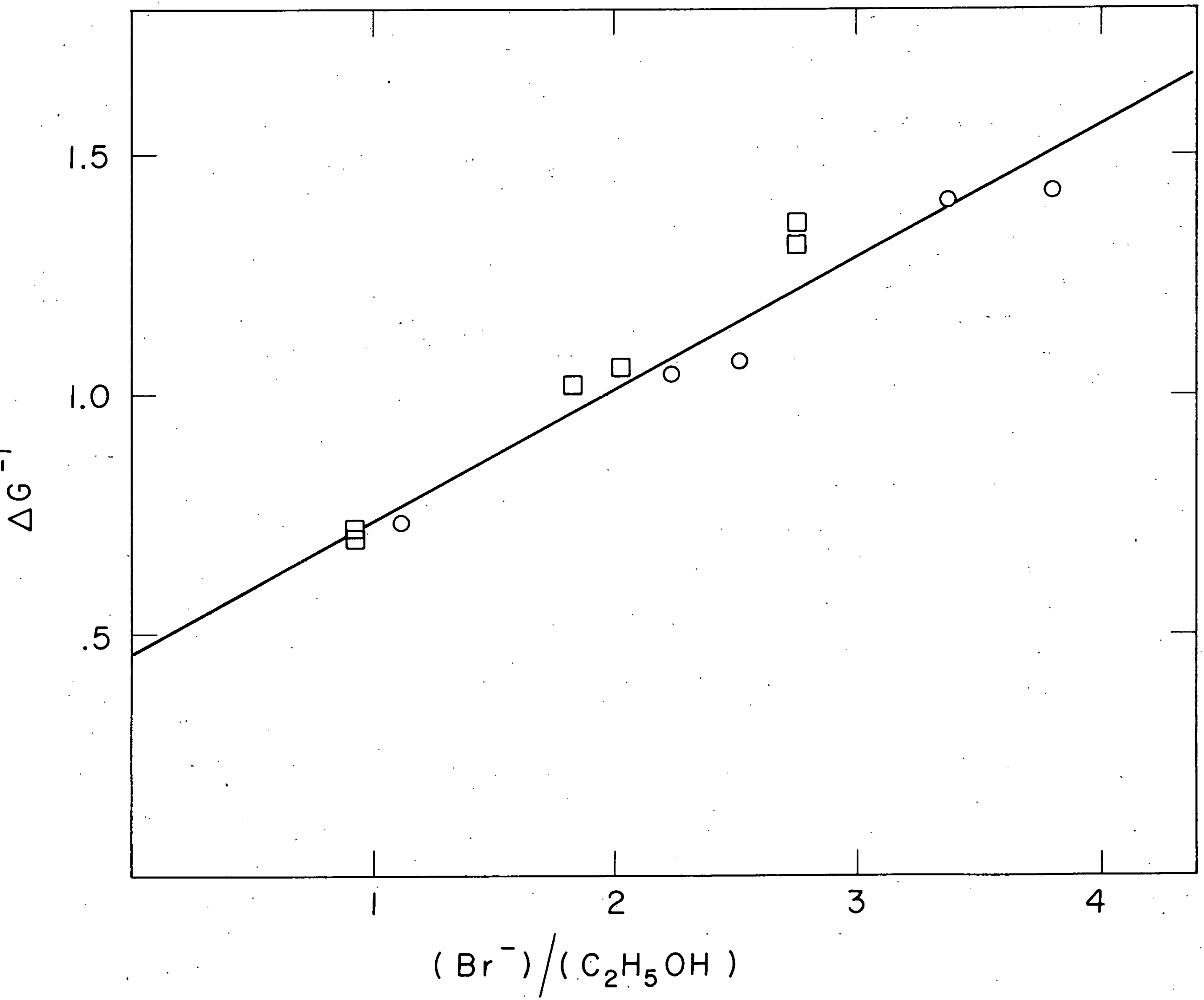
3
4
(Br^-) / (C_2H_5OH)


1.5
1.0
.5
ΔG^{-1}
1
2
3
4
$(Br^-)/(C_2H_5OH)$