# Effect of Pressure on the Rates of Reaction of Solvated Electrons and Hydrogen Atoms in Liquid Methanol[1]

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**Abstract:** The yield of hydrogen at 296°K from neutral methanol and 0.5 m*M* perchloric acid in methanol was $g(H_2) = 5.45$, independent of pressure in the range 1 bar to 5.4 kbar. In 0.10 *M* perchloric acid in methanol, $g(H_2) = 6.25$ at 1 bar and 6.00 at 5.4 kbar were measured. The efficiencies of scavenging free ion solvated electrons by nitrobenzene in neutral and acidic methanol, and by acetone in neutral methanol, decreased greatly with increase in pressure. The corresponding efficiencies of scavenging in the spurs were little affected by pressure. The following rate constant ratios at 1 bar and differences of volumes of activation were measured: $e^-_{solv} \rightarrow CH_3O^-_{solv} + H$ (9), $e^-_{solv} + S \rightarrow S^-_{solv}$ (12), $e^-_{solv} + H^+_{solv} \rightarrow H$ (5); $k_{12}/k_9 = 4.3 \times 10^4\ M^{-1}$ for nitrobenzene and $1.7 \times 10^4\ M^{-1}$ for acetone, $\Delta V_{12}^{\ddagger} - \Delta V_9^{\ddagger} = 15$ cm$^3$/mol for both solutes; $k_5/k_{12} = 3.9$ when S is nitrobenzene, $\Delta V_5^{\ddagger} - \Delta V_{12}^{\ddagger} = -3$ cm$^3$/mol, adjusted to zero ionic strength. The free ion yield in methanol is $g(e^-_{solv})_{fi} = 1.8 \pm 0.1$ at 1 bar and 1.9 at 5.4 kbar. The density-normalized range of the secondary electrons in methanol at 296°K is $bd = 1.4 \times 10^{-7}$ g/cm$^2$, independent of pressure. Competition between the reactions $H + CH_3OH \rightarrow H_2 + CH_2OH$ (10) and $H + S \rightarrow HS$ (21) was studied at 296°K at 1 bar and 5.4 kbar. Values of $k_{21}/k_{10}$ at 1 bar and $(\Delta V_{21}^{\ddagger} - \Delta V_{10}^{\ddagger})$ averaged between 1 bar and 5.4 kbar for two solutes S are: cyclohexene, 430, +2.0 cm$^3$/mol; phenol, 130, −2.0 cm$^3$/mol. The volume of activation of hydrogen atom addition to the aromatic ring is 4 cm$^3$/mol more negative than that of addition to a monoolefin. Rate constants of reaction of solvated electrons with several solutes at 295°K, measured by the pulse-radiolysis-spectroscopy technique, are $M^{-1}$ sec$^{-1}$: cyclohexene, $<1 \times 10^4$; hexene-1, $1 \times 10^5$; benzene, $1 \times 10^6$; phenol, $7 \times 10^6$. The phenol reaction with $e^-_{solv}$ produces hydrogen, perhaps *via* $C_6H_5OH^-_{solv} \rightarrow H + C_6H_5O^-_{solv}$ (4). The hydrogen yields from pure acetone were $g(H_2) = 0.90$ at 1 bar and 0.55 at 5.4 kbar, while that from pure cyclohexene $g(H_2) = 1.2$ independent of pressure.

The effect of pressure upon the behavior of radiolysis intermediates in liquids is being pursued in several laboratories employing competition kinetics[2-8] and high pressure pulse spectroscopy.[9-11]

A correlation between the entropies of activation and volumes of activation for the self-decomposition of solvated electrons in ethanol[7] and water[5] has been established by using both competition kinetics[5,7,12] and pulse-spectroscopy[10] at different temperatures[12,13] and pressures[5,7,10]

$$e^-_{solv} \longrightarrow RO^-_{solv} + H \qquad (1)$$

where R is either an alkyl group or a hydrogen atom.

In ethanol it was observed that the free ion yield $g(e^-_{solv})_{fi}$ was independent of pressure, and the ratio of the diffusion coefficient of solvated protons to that of solvated electrons increased markedly with increasing pressure.[7]

For the hydrogen atom reactions 2 and 3 in ethanol

$$H + C_2H_5OH \longrightarrow H_2 + CH_3CHOH \qquad (2)$$

$$H + S \longrightarrow HS \qquad (3)$$

the value of $k_3/k_2$ decreased with increasing pressure when S was an olefin, whereas the effect of pressure was opposite when S was phenol or benzene.[7]

An interesting observation was that a reaction of solvated electrons with phenol produced hydrogen, presumably through (4).

$$C_6H_5OH^-_{solv} \longrightarrow C_6H_5O^-_{solv} + H \qquad (4)$$

To test these observations further, methanol was chosen as solvent. The advantage of using methanol is that its radiolysis does not produce a scavenger for solvated electrons, in contrast to ethanol which produces acetaldehyde. As a result, some of the conclusions drawn from the ethanol system were indirect.[7] Methanol promises to be a less complicated system, which will allow more precise information to be obtained.

## Experimental Section

Absolute methanol, analyzed reagent spectrophotometric grade from Baker Chemical Co., was refluxed for 12 hr after addition of 2 g of 2,4-dinitrophenylhydrazine and 0.5 g of concentrated sulfuric acid to 1 l. of the alcohol. The refluxing system was rinsed with the absolute methanol before filling and was flushed with ultrahigh purity argon (Matheson) before and during refluxing. The alcohol was then distilled and the middle fraction collected.

Reagent grade nitrobenzene from Fisher Scientific Co. was distilled before use. Baker analyzed reagent spectrophotometric grade acetone, analytical reagent grade phenol from B.D.H. Chemicals, and Baker and Adamson analytical reagent grade perchloric acid (mol ratio $HClO_4/H_2O = 1/2$) were used as received. Phillips Research grade cyclohexene was stirred with sodium-potassium alloy under vacuum for about 40 hr to remove electron-scavenging impurities, then distilled into evacuated ampoules, sealed off, and stored in the dark. These ampoules were opened just prior to use to avoid peroxide formation.

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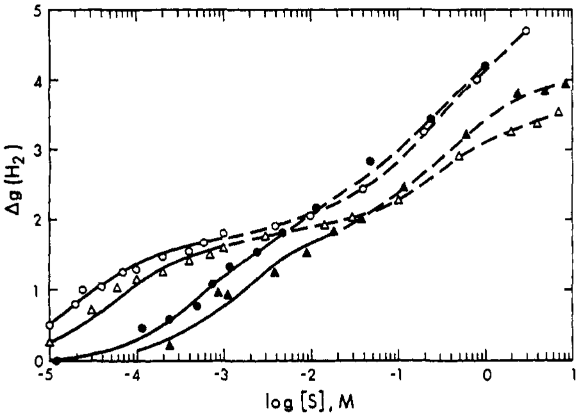

Figure 1. $\Delta g(H_2)$ from neutral methanol as a function of solute S concentration: nitrobenzene (O); acetone (Δ). Open symbols, 1 bar; filled symbols, 5.4 kbar. The solid lines were calculated using eq 14. The broken lines are empirical.

The techniques used for steady state radiolysis and product analysis have been described elsewhere.[1,6–8] Irradiation was performed at 296°K with a $^{60}Co$ Gamma source (Atomic Energy of Canada Ltd.) at a dose rate of $1 \times 10^{17}$ eV/(g min) in methanol. The dose was $2 \times 10^{18}$ eV/g. The amount of sample used was 2.37 g at 1 bar and 2.84 g at 5.4 kbar.

For neutral methanol, both syringe and goosenecked cells[6] were used to determine the hydrogen yields at 1 bar and 5.4 kbar. The hydrogen yields from these two techniques agreed with each other. For the rest of the experiments only the syringe technique[6] was used. Solutions of known concentrations of scavengers were prepared volumetrically or gravimetrically.

Rate constants for several reactions of solvated electrons were measure by pulse-radiolysis spectroscopy as described earlier.[8,14] The 0.1 μsec pulses of 1.7 MeV electrons delivered $3 \times 10^{16}$ eV/g. The temperature was 295°K.

## Results

**Pure and Acidic Methanol.** The yield of hydrogen from neutral methanol was $g(H_2) = 5.45$ independent of pressure over the range 1 bar to 5.4 kbar. This value is in agreement with previously published values at atmospheric pressure.[15–17]

The values of $g(H_2)$ from the acidic solutions were 5.45 for 0.1 and 0.5 m*M*, independent of pressure, and 6.25 and 6.00 from 0.10 *M* perchloric acid solutions at 1 bar and 5.4 kbar, respectively.

**Scavenger Solutions.** Yields from the scavenging studies were based on the energy initially absorbed in the solvent only: $g(H_2) = g(H_2)/\epsilon_s$, where $\epsilon_s$ is the electron fraction of solvent, including the acid when present. The yields from the acetone solutions were corrected for the direct radiolysis of acetone using $g(H_2) = 0.90$[18] at 1 bar and 0.55 at 5.4 kbar, while those from cyclohexene solutions were corrected using $g(H_2) = 1.2$[19] independent of pressure. The hydrogen yields from the direct radiolysis of nitrobenzene and phenol are so low that no correction was necessary.[20]

The decrease in the hydrogen yield, $\Delta g(H_2) = [g(H_2)_0 - g(H_2)]$, plotted against the molar concentrations of nitrobenzene and acetone in neutral methanol at 1 bar and 5.4 kbar, is presented in Figure 1. The efficiency of scavenging hydrogen precursors by nitrobenzene or acetone at low concentrations decreases with increasing pressure, whereas the pressure effect on such reactions at high concentrations is smaller and complex (Figure 1).

Concentrations of nitrobenzene greater than 1 *M* could not be used at the high pressure because precipitation occurred.

The yields of hydrogen at a fixed molar concentration of nitrobenzene or acetone were measured as a function of pressure between 1 bar and 5.4 kbar. The results obtained are presented in Table I.

**Table I.** Pressure Effect on $g(H_2)$ from Nitrobenzene or Acetone Solutions in Neutral Methanol

| [Nitrobenzene] = $5.0 \times 10^{-4}$ *M*[a] | | [Acetone] = $1.0 \times 10^{-3}$ *M*[a] | |
|---|---|---|---|
| *P*, kbar | $g(H_2)$ | *P*, kbar | $g(H_2)$ |
| 0 | 3.85 | 0 | 3.91 |
| 1.23 | 3.94 | 1.05 | 4.03 |
| 1.72 | 4.02 | 2.10 | 4.14 |
| 2.45 | 4.21 | 3.10 | 4.36 |
| 3.70 | 4.37 | 4.05 | 4.55 |
| 5.47 | 4.70 | 5.43 | 4.84 |

[a] Concentrations were kept constant by adjusting for the compressibility of the solvent.

A study was made of the competition between acid and nitrobenzene for solvated electron free ions at 1 bar and 5 kbar. The hydrogen yields are given in Table II. The values of $g(H_2)$ are between those caused by the presence of either solute alone.

**Table II.** The Yield of Hydrogen as a Function of Nitrobenzene Concentration from Acidic Methanol at 1 bar and 5.4 kbar

| 1 bar<br>[HClO$_4$] = $1.0 \times 10^{-4}$ *M* | | 5.4 kbar<br>[HClO$_4$] = $5.0 \times 10^{-4}$ *M* | |
|---|---|---|---|
| [Nitrobenzene], *M* | $g(H_2)$ | [Nitrobenzene], *M* | $g(H_2)$ |
| 0 | 5.45 | 0 | 5.45 |
| $8.0 \times 10^{-5}$ | 5.37 | $8.7 \times 10^{-4}$ | 5.07 |
| $1.00 \times 10^{-4}$ | 5.03 | $9.9 \times 10^{-4}$ | 4.98 |
| $2.00 \times 10^{-4}$ | 4.83 | $1.50 \times 10^{-3}$ | 4.77 |
| $2.80 \times 10^{-4}$ | 4.72 | $1.80 \times 10^{-3}$ | 4.74 |
| $4.0 \times 10^{-4}$ | 4.36 | $2.48 \times 10^{-3}$ | 4.52 |
| $6.0 \times 10^{-4}$ | 4.39 | $4.96 \times 10^{-3}$ | 4.32 |
| $8.0 \times 10^{-4}$ | 4.19 | $7.44 \times 10^{-3}$ | 3.87 |
| $1.20 \times 10^{-3}$ | 3.92 | | |

The dissociation constant of perchloric acid in 2-propanol, $K(HClO_4)_{2\text{-PrOH}} = 1.6 \times 10^{-2}$ *M*, has been reported.[21] The dissociation constant of perchloric acid in methanol is greater than $1.6 \times 10^{-2}$ *M*, because the acid dissociation constant increases with increasing dielectric constant of the solvent.[22] The perchloric acid was completely dissociated in the concentration range used for the competition with nitrobenzene.

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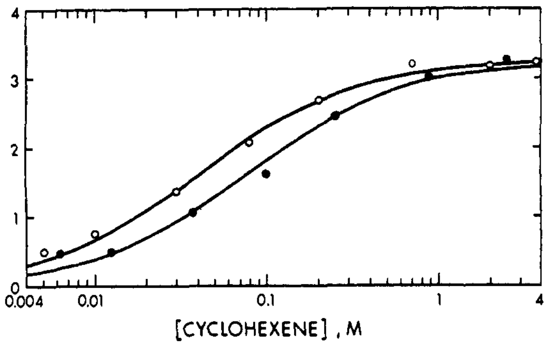

Figure 2. $\Delta g(H_2)$ from neutral methanol as a function of cyclohexene concentration: (○) 1 bar; (●) 5.4 kbar. The curves were calculated from eq 23.

Figure 2 displays $\Delta g(H_2)$ as a function of cyclohexene concentration in neutral methanol at 1 bar and 5.4 kbar. It is evident from Figure 2 that the efficiency of scavenging hydrogen precursors by cyclohexene decreases with increasing pressure.

The effect of phenol on the hydrogen yields from neutral methanol is shown in Figure 3. The scavenging efficiency of phenol increases with increasing pressure.

To simplify the study of hydrogen atom reactions, 0.10 *M* perchloric acid in methanol was used as the solvent. In such solutions the solvated electrons were rapidly converted to hydrogen atoms by reaction 5.

$$e^-_{solv} + H^+_{solv} \longrightarrow H \qquad (5)$$

The effects of phenol on the hydrogen yields from the acidic solutions are depicted in Figure 4. The effect of pressure on the scavenging efficiency of phenol in acidic solutions is similar to that on neutral solutions (Figures 3 and 4).

**Values of $k(e^-_{solv} + S)$.** The rate constants for solvated-electron reactions with the solutes used in this work were measured at 1 bar by the pulse-radiolysis-spectroscopy technique and are listed in Table III.

**Table III.** Solvated Electron Reaction Rate Constants in Methanol at 295°K and 1 bar

| Solute | $k$, $M^{-1}$ sec$^{-1}$ |
|---|---|
| Nitrobenzene | $2.0 \times 10^{10}$ [a] |
| Acetone | $4.2 \times 10^{9}$ [a] |
| Perchloric acid | $6.5 \times 10^{10}$ [b] |
| Cyclohexene | $<1 \times 10^{4}$ |
| Hexene-1 | $1 \times 10^{5}$ |
| Benzene | $1 \times 10^{6}$ |
| Phenol | $7 \times 10^{6}$ |
| None | $2 \times 10^{5}$ sec$^{-1}$ [a] |

[a] Reference 13. [b] Reference 14.

## Discussion

**Pure Methanol.** The mechanism of hydrogen formation in the $\gamma$ radiolysis of liquid methanol may be represented as follows.[17] Square brackets around reactants or products denote that the species are inside a spur

$$m\mathrm{CH_3OH} \rightsquigarrow [H^+_{solv}, e^-_{solv}, H, HCHO, CH_3O] \qquad (6)$$

$$[H^+_{solv} + e^-_{solv}] \longrightarrow [H + n\mathrm{CH_3OH}] \quad \text{(geminate neutralization)} \qquad (7)$$

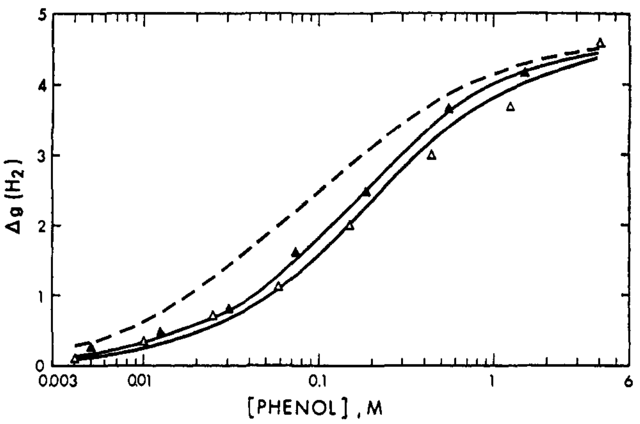

Figure 3. $\Delta g(H_2)$ from neutral methanol as a function of phenol concentration: (△) 1 bar; (▲) 5.4 kbar. The full curves were calculated from eq 23. The dashed curve refers to 1 bar and was calculated using eq 24.

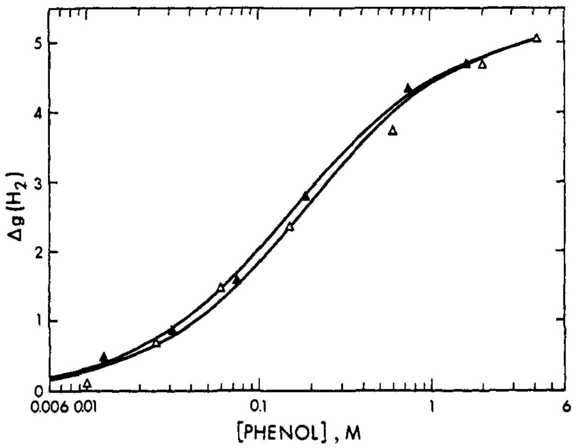

Figure 4. $\Delta g(H_2)$ from acidic methanol (0.10 *M* perchloric acid) as a function of phenol concentration: (△) 1 bar; (▲) 5.4 kbar. The curves were calculated using eq 23.

$$[H^+_{solv} + e^-_{solv}] \longrightarrow H^+_{solv} + e^-_{solv} \text{ (free ions)} \qquad (8)$$

$$e^-_{solv} \longrightarrow \mathrm{CH_3O^-_{solv}} + H \qquad (9)$$

$$H + \mathrm{CH_3OH} \longrightarrow H_2 + \mathrm{CH_2OH} \qquad (10)$$

$$H^+_{solv} + \mathrm{CH_3O^-_{solv}} \longrightarrow p\mathrm{CH_3OH} \qquad (11)$$

where $m$, $n$, and $p$ are integers.

## Solvated Electrons

**Scavengers in Neutral Methanol.** An electron scavenger S, such as nitrobenzene or acetone, in neutral methanol reduces the hydrogen yield by competing with reactions 7 and 9.

$$e^-_{solv} + S \longrightarrow S^-_{solv} \qquad (12)$$

$$S^-_{solv} + H^+_{solv} \longrightarrow SH \qquad (13)$$

Nitrobenzene and acetone at concentrations $<10^{-3}$ *M* react exclusively with free ions (Figure 1).[7,17] Free ion reactions involve homogeneous kinetics and the competition between (9) and (12) is described by (14).

$$[\Delta g(H_2)]^{-1} = [g(e^-_{solv})_{fi}]^{-1}\{1 + (k_9/k_{12}[S])\} \qquad (14)$$

Values of $g(e^-_{solv})_{fi}$ and $k_{12}/k_9$ were obtained from plots of $1/\Delta g(H_2)$ *vs.* $1/[S]$ for S concentrations $<10^{-3}$ *M* at 1 bar and $<10^{-2}$ *M* at 5.4 kbar (Figure 5). Higher concentrations of S were necessary at 5.4 kbar because of the greatly reduced scavenging efficiencies at high

Table IV. Kinetic Parameters for Electron Reactions in Methanol at 296°K

| [HClO$_4$], | | | 1 bar | | 5.4 kbar | | $\{(k_a/k_b)_{1\ \text{bar}}/$ | $\Delta V_a{}^{\ddagger} - \Delta V_b{}^{\ddagger}$, |
|---|---|---|---|---|---|---|---|---|
| $M$ | S | $k_a/k_b$ | $k_a/k_b$[a] | $g(e^-_{solv})_{fi}$[b] | $k_a/k_b$[a] | $g(e^-_{solv})_{fi}$[b] | $(k_a/k_b)_{5.4\ \text{kbar}}\}$ | cm$^3$/mol |
| 0 | Nitrobenzene | $k_{12}/k_9$ | $4.3 \times 10^4\ M^{-1}$ | 1.7 | $1.7 \times 10^3\ M^{-1}$ | 1.9 | 25 | 14.6 (15.1)[c] |
| 0 | Acetone | $k_{12}/k_9$ | $1.7 \times 10^4\ M^{-1}$ | 1.7 | $6.7 \times 10^2\ M^{-1}$ | 1.9 | 25 | 14.6 (14.9)[c] |
| $1.0 \times 10^{-4}$ | Nitrobenzene | $k_5/k_{12}$ | 3.7 (3.9)[d] | 1.9 | | | | |
| $5.0 \times 10^{-4}$ | Nitrobenzene | $k_5/k_{12}$ | | | 6.2 (7.4)[d] | 2.0 | 0.60 (0.53)[d] | −2.4 (−2.9)[d] |

[a] ±15%. [b] ±5%. [c] These values were computed from the plots of log $k_{12}/k_9$ vs. $P$ (Figure 6). [d] Adjusted to zero ionic strength (ref 25).

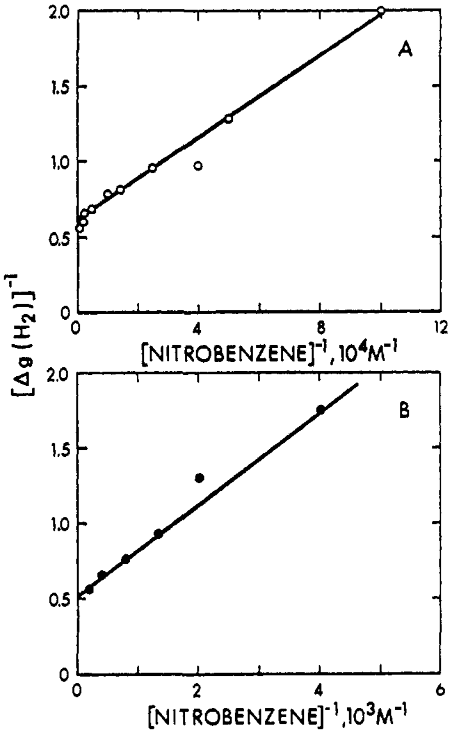

Figure 5. Plots of $\Delta g(H_2)^{-1}$ against [nitrobenzene]$^{-1}$ for neutral methanol [eq 14]: (A) 1 bar; (B) 5.4 kbar.

pressure (Figure 1). The values of $g(e^-_{solv})_{fi}$ were 1.7 ± 0.1 at 1 bar and 1.9 ± 0.1 at 5.4 kbar (Table IV). The values of $k_{12}/k_9$ for both nitrobenzene and acetone decreased with increasing pressure (Table IV).

Using eq 15[23] and the values of the ratio $k_{12}/k_9$ at 1 bar and 5.4 kbar, the difference between the volumes of activation of reactions 12 and 9 is estimated to be $\Delta V_{12}{}^{\ddagger} - \Delta V_9{}^{\ddagger} = 15$ cm$^3$/mol.

$$\log \frac{(k_a/k_b)_{P_1}}{(k_a/k_b)_{P_2}} = \frac{(P_2 - P_1)}{2.3RT}(\Delta V_a{}^{\ddagger} - \Delta V_b{}^{\ddagger}) \quad (15)$$

The upper end of the $\Delta g(H_2)$ curve for nitrobenzene is almost unaffected by pressure (Figure 1), which implies that the competition between reactions 7 and 16 in the spurs is independent of pressure, and $\Delta V_{16}{}^{\ddagger} - \Delta V_7{}^{\ddagger} \approx 0$.

$$[e^-_{solv} + S] \longrightarrow [S^-_{solv}] \quad (16)$$

The effect of acetone at high pressures appears to be complex (Figure 1).

**Scavenging Studies in Neutral Methanol.** The form of eq 14 used for neutral methanol solutions at different pressures was

$$(g(e^-_{solv})_{fi}/[g(H_2)_P - \{5.45 - g(e^-_{solv})_{fi}\}]) - 1 = k_{12}[S]/k_9 \quad (17)$$

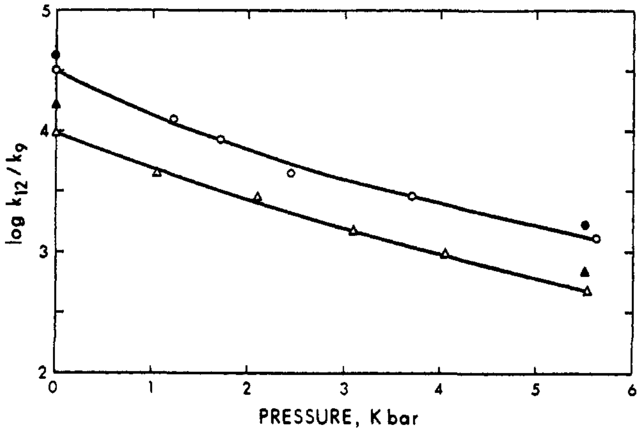

Figure 6. Plots of log $k_{12}/k_9$ against pressure in neutral methanol: (○) $5.0 \times 10^{-4}$ $M$ nitrobenzene; (△) $1.0 \times 10^{-3}$ $M$ acetone. The filled points were taken from Table IV.

where the $g(e^-_{solv})_{fi}$ values were assumed to vary proportionately to pressure between the experimentally estimated values 1.7 at 1 bar and 1.9 at 5.4 kbar (Table IV); $g(H_2)_P$ is the measured yield of hydrogen at pressure $P$ (Table I) and 5.45 is the $g$ value of hydrogen from pure methanol, independent of pressure.

Plots of log $k_{12}/k_9$ vs. $P$ (see eq 15, with $P_2$ = 1 bar) for nitrobenzene and acetone solutions are presented in Figure 6. The values of $k_{12}/k_9$ at 1 bar and 5.4 kbar listed in Table IV have been included in the plots. The curvature of the lines in Figure 6 indicates that the value of $\Delta V_{12}{}^{\ddagger} - \Delta V_9{}^{\ddagger}$ decreases with increasing pressure. The implications of such behavior have been discussed elsewhere.[24] The value of $\Delta V_{12}{}^{\ddagger} - \Delta V_9{}^{\ddagger}$ estimated from the slope between 1 bar and 5.4 kbar equals 15 cm$^3$/mol for both nitrobenzene and acetone. These values are in agreement with those listed in Table IV. At 1 bar, $\Delta V_{12}{}^{\ddagger} - \Delta V_9{}^{\ddagger} \approx 21$ cm$^3$/mol.

**Acidic Solutions.** The presence of both acid and nitrobenzene in methanol creates a competition between reactions 12 and 5.

$$e^-_{solv} + H^+_{solv} \longrightarrow H \quad (5)$$

The concentrations of $H^+_{solv}$ used were $1.00 \times 10^{-4}$ $M$ at 1 bar and $5.00 \times 10^{-4}$ $M$ at 5.4 kbar. Total concentrations of acid and nitrobenzene chosen were high enough that all free ion solvated electrons would undergo either (12) or (5), but low enough that there would be negligible scavenging in the spurs.[7,17]

Kinetic analysis of the results in Table II was done using eq 18.

$$[\Delta g(H_2)]^{-1} = [g(e^-_{solv})_{fi}]^{-1}\{1 + (k_5[H^+_{solv}]/k_{12}[S])\} \quad (18)$$

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Values of $k_5/k_{12}$ and $g(e^-_{solv})_{fi}$ at 1 bar and 5.4 kbar were obtained from the plots of $1/\Delta g(H_2)$ *vs.* $[H^+]/[S]$ in Figure 7 and are listed in Table IV.

The value of $k_5/k_{12}$ depends on the ionic strength of the solution.[25] For the neutral reactants nitrobenzene and nitrous oxide, $k_{12}$ should be essentially independent of ionic strength. The dependence of $k_5/k_{12}$ for nitrous oxide in methanol is known as a function of ionic strength.[25] The values of the ratio $k_5/k_{12}$ for nitrobenzene were corrected to zero ionic strength by using the same factors as those from corresponding acid–nitrous oxide competitions in methanol[25] and are listed in parentheses in Table IV. The analysis of the data according to eq 15 yields $\Delta V_5^{\ddagger} - \Delta V_{12}^{\ddagger} = -3$ cm³/mol (Table IV).

**Values of Volumes of Activation.** The volumes of activation for the diffusion of sodium picrate, sodium bromide, and hydrogen bromide in methanol at 25° are 6, 5, and 3 cm³/mol,[26] respectively, averaged between 1 and 3000 bar. The corresponding volume of activation for viscous flow is 7 cm³/mol,[26] which is 1–4 cm³/mol greater than those for diffusion of the above ionic solutes. The abnormally small $\Delta V_{diff}^{\ddagger}$ for hydrogen bromide is attributed to the "hopping" mechanism of diffusion of protons in alcohols and water.[7,26] One may therefore assume that $\Delta V^{\ddagger}$ for diffusion is normally about 2 cm³/mol smaller than that for viscous flow in methanol at a few kilobars of pressure.

The value of $k_{12} = 2.0 \times 10^{10}\ M^{-1}\ \sec^{-1}$ for nitrobenzene indicates that it is essentially diffusion controlled (calculate $k = 2 \times 10^{10}\ m^{-1}\ \sec^{-1}$ using diffusion coefficients $2 \times 10^{-5}$ cm²/sec for $e^-_{solv}$,[27] $1.8 \times 10^{-5}$ cm²/sec for nitrobenzene,[28] and a reaction encounter distance of 6 Å). The volume of activation for viscous flow, averaged between 1 bar and 5.4 kbar, is 6 cm³/mol,[29] so it is assumed that $\Delta V_{12}^{\ddagger} \approx 4$ cm³/mol for nitrobenzene. Combining this value with the measured $\Delta V_{12}^{\ddagger} - \Delta V_9^{\ddagger} = 15$ cm³/mol (Table IV), one obtains $\Delta V_9^{\ddagger} \approx -11$ cm³/mol, averaged between 1 bar and 5.4 kbar. From $\Delta V_5^{\ddagger} - \Delta V_{12}^{\ddagger} = -3$ cm³/mol, one obtains $\Delta V_5^{\ddagger} \approx 1$ cm³/mol. The negative value of $\Delta V_5^{\ddagger} - \Delta V_{12}^{\ddagger}$ implies an abnormally low value of $\Delta V_{diff}^{\ddagger}(H^+)$, in support of the conclusion drawn from the measurement of diffusion coefficients of HBr and NaBr.[26]

**Pressure Dependence of $g_{fi}$ and Secondary Electron Range. Model Calculations.** The free ion yield can be calculated from eq 19[30]

$$g_{fi} = g_{tot}\int_0^{\infty} F(y) \exp(-\xi^2/\epsilon kTy)\mathrm{d}y \qquad (19)$$

where $g_{tot}$ is the total ionization yield, $F(y)\mathrm{d}y$ is the fraction of thermalized electron–ion pairs that have initial intrapair distances between $y$ and $y + \mathrm{d}y$, $\xi$ is the electron charge, $\epsilon$ is the dielectric constant of the liquid, $k$ is Boltzmann's constant, and $T$ is the absolute temperature.

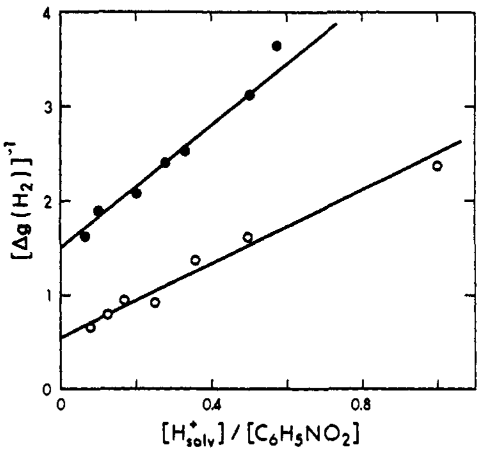

Figure 7. Plots of $\Delta g(H_2)^{-1}$ against $[H^+_{solv}]$/[nitrobenzene] in acidic methanol [eq 18]: (○) $[H^+_{solv}] = 1.0 \times 10^{-4}\ M$ at 1 bar; (●) $[H^+_{solv}] = 5.0 \times 10^{-4}\ M$ at 5.4 kbar (displaced vertically by 1.0 units for clarity).

Table V. Pressure Dependence of $g_{fi}$ and Most Probable Range $b$ of the Electrons in Methanol at 296°K

| | 1 bar | 5.4 kbar |
|---|---|---|
| $g_{fi}$ | 1.8[a] | 1.9[a] |
| $g_{tot}$ | 4.6[b] | 4.6[b] |
| $\epsilon$ | 33.1 | 42.5[c] |
| $d$, g/cm³ | 0.789 | 0.978[d] |
| $b$, Å | 17.5 | 14.5 |
| bd, $10^{-8}$ g/cm² | 13.8 | 14.2 |

[a] Average of the values in Table IV. [b] Reference 17, assumed to be independent of pressure. [c] Extrapolated from results up to 3 kbar in S. Kyropoulos, *Z. Phys.*, **40**, 507 (1926), with the aid of values for ethanol up to 6 kbar reported by W. E. Danforth, Jr., *Phys. Rev.*, **38**, 1224 (1931). [d] Reference 29, p 128.

Using the Gaussian function (eq 20) for $F(y)$ in (19) and the values of $g_{tot}$, $\epsilon$, and $T$ listed in Table V, one obtains the most probable electron range $b = 17.5$ Å at 1 bar and 14.5 Å at 5.4 kbar.

$$F(y) = (4y^2/\pi^{1/2}b^3) \exp(-y^2/b^2) \qquad (20)$$

$b$ is the dispersion parameter and the most probable electron range in this distribution. The density-normalized range bd is $1.4 \times 10^{-7}$ g/cm² at 296°K, independent of pressure (Table V).

The density-normalized range of the electrons in ethanol at 296°K is $1.9 \times 10^{-7}$ g/cm², also independent of pressure.[7] The ranges of these secondary electrons in alcohols simply vary inversely as the density when the liquid is compressed. If changes in the amount of order in the methanol liquid structure occur with the 24% reduction of volume at 5.4 kbar, such as an increase in the average length of the hydrogen bonded chains,[31] they do not affect the efficiencies of the electron energy loss and localization processes. The simple density effect is consistent with a multibody-scattering picture of electron localization.[32]

## Hydrogen Atoms

**Cyclohexene in Neutral Methanol.** Cyclohexene scavenges hydrogen atoms.[33,34] It does not react signifi-

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**Table VI.** Kinetic Parameters of Hydrogen Atom Reactions in Methanol at 296°K

| [HClO$_4$], *M* | S | 1 bar $k_{21}/k_{10}$ | 1 bar $k_{22}/k_{21}$ | 1 bar $\Delta g(H_2)_{max}$ | 5.4 kbar $k_{21}/k_{10}$ | 5.4 kbar $k_{22}/k_{21}$ | 5.4 kbar $\Delta g(H_2)_{max}$ | $\Delta V_{21}^{\ddagger} - \Delta V_{10}^{\ddagger}$,[a] cm$^3$/mol | $\Delta V_{22}^{\ddagger} - \Delta V_{21}^{\ddagger}$, cm$^3$/mol |
|---|---|---|---|---|---|---|---|---|---|
| 0 | Cyclohexene | 430 | 0.44 | 4.6 | 276 | 0.44 | 4.6 | +2.0 | 0.0 |
| 0 | Phenol | 130 | 0.0[b] | 4.6 | 200 | 0.0 | 4.6 | −2.0 | |
| 0.1 | Phenol | 130 | 0.0[b] | 5.3 | 200 | 0.0 | 5.1 | −2.0 | |

[a] Average value between 1 bar and 5.4 kbar. [b] Assumed.

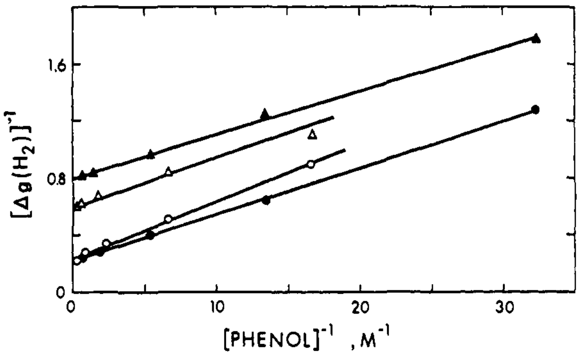

Figure 8. Plots of $\Delta g(H_2)^{-1}$ against $[phenol]^{-1}$ in neutral and acidic methanol [eq 23]: neutral methanol (○); acidic methanol (△). Open symbols, 1 bar; filled symbols, 5.4 kbar. △ and ▲ displaced vertically by 0.4 and 0.6 unit, respectively, for clarity.

cantly with solvated electrons in methanol (Table III) or ethanol.[7] Thus, in cyclohexene solutions reactions 21 and 22 compete with reaction 10

$$H + S \longrightarrow SH \qquad (21)$$

$$H + S \longrightarrow H_2 + R' \qquad (22)$$

where S represents a solute, in this case cyclohexene.

The curves in Figure 2 were calculated using eq 23.

$$\frac{1}{\Delta g(H_2)} = \frac{1}{\Delta g(H_2)_{max}}\left\{1 + \frac{k_{10}[CH_3OH]}{k_{21}[S]} + \frac{k_{22}}{k_{21}}\right\} \qquad (23)$$

The value of $\Delta g(H_2)_{max} = 4.6$ was obtained from solutions of phenol in neutral methanol assuming that $k_{22}/k_{21} = 0$ for phenol (Table VI and Figure 8). The values of $k_{21}/k_{10}$ and $k_{22}/k_{21}$ were estimated from plots of $1/\Delta g(H_2)$ *vs.* 1/[S], such as those in Figure 8, and are listed in Table VI. The concentrations of pure methanol are 24.6 *M* at 1 bar and 30.6 *M* at 5.4 kbar. Probable errors in estimating $\Delta g(H_2)_{max}$ and the rate constant ratios are ±4 and ±10%, respectively.

The value $k_{22}/k_{21} = 0.44$ obtained for cyclohexene in methanol at 1 bar and 5.4 kbar (Table VI) is similar to the value 0.52 reported for the same solute in ethanol.[8]

Equation 15 was used to estimate the differences in the volumes of activation from the values of the rate constant ratios at 1 bar and 5.4 kbar (Table VI). The values $\Delta V_{21}^{\ddagger} - \Delta V_{10}^{\ddagger} = +2.0$ cm$^3$/mol and $\Delta V_{22}^{\ddagger} - \Delta V_{21}^{\ddagger} = 0$ were obtained. These values are similar to those obtained in ethanol.[8] The difference between the volumes of activation of abstraction and addition reactions of hydrogen atoms with hexene-1 in *n*-hexane has also been found to be approximately zero.[6]

**Phenol in Neutral Methanol.** Phenol has been reported to react with electrons[7,35] as well as with hydrogen atoms.[36] It has been shown recently that the apparent reactivities of phenol and benzene with electrons in ethanol are much less in competition kinetics than those measured by pulse-radiolysis spectroscopy.[8] The present results obtained from competition reactions were treated according to eq 23. Values of $\Delta g(H_2)_{max}$ and $k_{21}/k_{10}$ were obtained from plots of $1/\Delta g$ (Hz) *vs.* 1/[S] (Figure 8) and are presented in Table VI. The solid curves in Figure 3 were calculated using eq 23. The agreement between experimental points and calculated curves is good at both pressures. The dashed curve in Figure 3 was calculated using the hydrogen atom rate constant ratios given in Table VI and the solvated electron rate constants in Table III (1 bar). The total reduction in hydrogen yield was taken as the sum of the yields of scavenged electrons and hydrogen atoms, eq 24.

$$\Delta g(H_2) = g(e^-_{solv})_{scav} + g(H)_{scav} \qquad (24)$$

The yield of scavenged electrons was calculated using eq 14, while the yield of scavenged hydrogen atoms was estimated from eq 23. The values of $g(e^-_{solv})_{fi} = 1.8$ and $\Delta g(H_2)_{max} = [4.6 - g(e^-_{solv})_{scav}]$ were used in eq 14 and 23, respectively.

The curve calculated using (24) was too high (Figure 3), which suggests that reaction 4 takes place in phenolic solutions of methanol.

$$C_6H_5OH^-_{solv} \longrightarrow C_6H_5O^-_{solv} + H \qquad (4)$$

A similar conclusion was drawn in the ethanol study.[8] It is important to note that postulation of reaction of quasifree (dry) electrons with phenol would make the above discrepancies worse. No indication of reaction of quasifree electrons with solutes was obtained in either the ethanol[8] or methanol investigation.

The scavenging efficiency of phenol increased with increasing pressure, while that of cyclohexene decreased (Table VI). The volume of activation for hydrogen atom addition to phenol is 4 cm$^3$/mol more negative than that for addition to cyclohexene. The more negative value is probably related to the lower rate constant and to a more negative entropy of activation.[37]

**Phenol in Acidic Methanol (0.1 *M* HClO$_4$).** In strongly acidic methanol, reactions 7 and 9 are replaced by reaction 5. The results in Figure 4 are plotted according to eq 23 in Figure 8. The values of $\Delta g(H_2)_{max}$ and $k_{21}/k_{10}$ so obtained are presented in Table VI. The values of $k_{21}/k_{10}$ are the same as those obtained for neutral methanol. This supports the suggestion that solvated electrons reacting with phenol eventually produce hydrogen *via* reaction 4.

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