giving a good description of the experimental data...

2. A staged reaction scheme is proposed on the assumption that the reaction is a chain process; this scheme takes into account the interaction of the original substances and the intermediate species with the acidic centers of the catalyst. This scheme leads to a kinetic equation that coincides with the experimentally determined equation.

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KINETIC RELATIONSHIPS IN FORMATION OF ISOPRENE FROM EQUILIBRIUM

MIXTURE OF 3-METHYL-1-BUTEN-3-OL AND 3-METHYL-2-BUTEN-1-OL IN

AQUEOUS PERCHLORIC ACID SOLUTIONS

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3-Methyl-1-buten-3-ol (or dimethylvinylcarbinol, DMVC) and 3-methyl-2-buten-1-ol (or dimethylallyl alcohol, DMAA), which are obtained in the synthesis of 4,4-dimethyl-1,3-dioxane from isobutylene and formaldehyde [1], are readily dehydrated in acidic media forming isoprene $i-C_5H_8$ [2, 3].

The reversible isomerization of DMVC to DMAA proceeds in an acidic medium much more rapidly than the dehydration of the equilibrium mixture of DMVC and DMAA to $i-C_{5}H_{e}$ [3-6]. When the DMVC is heated in 4-7% + aqueous H_2SO_4 solutions at $70-90^{\circ}C$, the main reaction product is i-C₅H₈ [3]. The DMVC is also dehydrated when subjected to the catalytic action of KU-2 ion-exchange resin [7].

In [8], the kinetics and mechanism of i-C₅H₈ formation from an equilibrium mixture of DMVC and DMAA were investigated in 4.3-35.0% aqueous H₂SO₄ solutions at 25°C in a homogeneous reaction mixture. The initial DMVC concentrations ranged from 10⁻⁵ to 10⁻⁴ mole/liter. It was shown that under these conditions, the DMVC and DMAA dehydration is an equilibrium reaction, and the equilibrium concentration of isoprene depends on the concentration of H2SO4 in the solution. The ratio of the sum of the equilibrium concentrations of DMVC and DMAA (Cb^w) to the equilibrium concentration of i-C₅H₈ (C_1^{∞}) decreases from 15.8 to 7.2 as the H₂SO₄ concentration is raised from 4.3% to 39.2%.

†All concentrations are given in % by weight.

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It was shown in [8] that in the dehydration of these alcohols, the reaction complex and the activated complex consist of protonated molecules of the alcohol and a nucleophile. The nucleophiles are molecules of water from the solvate shell of the alcohol (pathway a) and anions of the acid (pathway b). According to [8], the influence of the medium on the effective rate constant for dehydration of the equilibrium mixture of DMVC and DMAA are described by the equation

$$k_{\rm d}^{\rm P} = k_{\rm d}^{\rm a} h_0 + k_{\rm d}^{\rm Nu} h_0 C_{\rm Nu} \tag{1}$$

where k_d^a and k_d^{Nu} are the specific rate constants for the reactions of dehydration along pathways a and b, respectively; C_{Nu} is the total concentration of nucleophiles, i.e., HSO₄⁻ and SO₄²⁻ anions, moles/liter; h₀ is the acidity of the medium.

The influence of the medium on the effective rate constant for hydration of $i-C_sH_8$ in H_2SO_4 is described by the equation

$$k_{\rm h} = K_{\rm deh} k_{\rm d} a_{\rm H_{20}} \frac{f_{i-{\rm C}_{\rm s}{\rm H}_{\rm s}}}{f_{\rm ROH}} = k_{\rm h}^{\rm a} a_{\rm H_{20}} h_0 + k_{\rm h}^{\rm Nu} a_{\rm H_{20}} h_0 C_{\rm Nu}$$
(2)

where $K_{deh} = C_b {}^{\infty}f_{ROH} / C_i {}^{\infty}a_{H_20}f_{i-C_5H_8}$; a_{H_20} is the activity of water in the solution; k_h^a and k_h^{Nu} are the specific rate constants for hydration of $i-C_5H_8$ through pathways a and b, respectively.

It was of interest to determine the influence of ClO_4 anions in the same reactions. It is known that ClO_4 anions do not manifest any nucleophilic effect in the hydrolysis of onitroformanilide (up to 60% HClO₄) [9] on the hydrolysis of formic acid esters (in moderately concentrated HClO₄ solutions) [10]. When these reactions are carried out in aqueous H₂SO₄ solutions, nucleophilic catalysis by the anions of the acid is manifested [9, 10].

Here we are reporting on a study of the kinetic relationships in the dehydration of DMVC and DMAA and the hydration of $i-C_{5}H_{8}$ in aqueous HClO₄.

EXPERIMENTAL

The original reactant was DMVC containing 99.33% of the principal substance and 0.56% water, bp 97.3°C. The original solution of HClO₄ (grade "o.ch." [extra-purity]) contained 58.6% HClO₄ as determined by titration with caustic. Solutions with the required concentrations were prepared by diluting the original solution (by weight) with double-distilled water. The concentration of the original DMVC was varied from 1.1 × 10⁻⁴ to 2.9 × 10⁻⁴ mole/ liter. The isoprene concentrations C₁ were determined from the maximal optical density on the kinetic curve and the molar extinction coefficient of i-C₅H₈ in 5% H₂SO₄ ($\epsilon_{227} = 1.54 \times 10^4$ liters/mole·cm). The sum of the equilibrium concentration and C₁[∞]. The section of the kinetic curve from the moment the reactant is introduced into the acid solution until equilibrium of the i-C₅H₈ with the DMVC and DMAA is reached is well described by an equation for reversible first-order reactions, and the effective rate constant k_{eff} that is obtained is equal to the sum of the effective rate constant k_{eff} that is obtained is equal to the sum of the effective rate constant for the alcohols and hydration of i-C₅H₈.

$$\begin{bmatrix} Me & Me \\ C-CH=CH_2 \rightleftharpoons G=CH-CH_2OH \\ Me & OH & Me \end{bmatrix} \xrightarrow{k_d \atop k_h} C-CH=CH_2+H_2O$$
(3)

The effective rate constants k_d and k_h were calculated individually as in [8].

DISCUSSION OF RESULTS

In HClO₄ solutions that are not too concentrated, an equilibrium mixture of DMVC, DMAA, and $i-C_5H_8$ is formed, without any side reactions. We also obtained kinetic curves for the formation of $i-C_5H_8$ in more concentrated aqueous HClO₄ solutions at 25°C. Judging by the chromatographic data, a byproduct (unidentified) is formed in solutions with HClO₄ concentrations greater than 30%, and hence the results from these experiments are not included in the data we have listed in Table 1.

TABLE 1. Data on the Dehydration of 3-Methyl-1-buten-3-ol and 3-Methyl-2-buten-1-ol and on the Hydration of Isoprene in Aqueous HClO₄ Solutions at 25°C

| HClO4, % | $c_{\rm b}^{\infty}/c_{\rm i}^{\infty}$ | ^k ef, | ₽'n, | ^k d, | K_{1} , $f_{i-C_{6}H_{8}}$ |
|---|--|---|---|---|--|
| | | min ⁻¹ | | | ^{*deh} /ROH |
| 2,44 4,99 5,99 11,98 16,97 17,92 20,04 23,88 26,96 29,95 | $\begin{array}{c} 15,0\\ 14,0\\ 13,5\\ 11,2\\ 10,5\\ 10,5\\ 10,3\\ 10,1\\ 9,9\\ 9,8 \end{array}$ | $\begin{array}{c} 4,3\cdot10^{-4}\\ 9,5\cdot10^{-4}\\ 1,9\cdot10^{-3}\\ 6,4\cdot10^{-3}\\ 1,2\cdot10^{-2}\\ 1,6\cdot10^{-2}\\ 2,6\cdot10^{-2}\\ 4,7\cdot10^{-2}\\ 8,1\cdot10^{-2}\\ 14,6\cdot10^{-2}\\ \end{array}$ | $\begin{array}{c} 2.7\cdot 10^{-5} \\ 6.3\cdot 10^{-5} \\ 1.3\cdot 10^{-4} \\ 5.2\cdot 10^{-4} \\ 1.0\cdot 10^{-3} \\ 1.4\cdot 10^{-3} \\ 2.3\cdot 10^{-3} \\ 4.2\cdot 10^{-3} \\ 7.4\cdot 10^{-3} \\ 1.3\cdot 10^{-2} \end{array}$ | $\begin{array}{c} 4.0\cdot10^{-4}\\ 8.9\cdot10^{-4}\\ 1.8\cdot10^{-3}\\ 5.9\cdot10^{-3}\\ 1.1\cdot10^{-2}\\ 1.5\cdot10^{-2}\\ 2.4\cdot10^{-2}\\ 4.3\cdot10^{-2}\\ 7.4\cdot10^{-2}\\ 0.133\end{array}$ | $\begin{array}{c} 1,0\\ 0,94\\ 0,91\\ 0,78\\ 0,76\\ 0,78\\ 0,76\\ 0,78\\ 0,76\\ 0,78\\ 0,80\\ 0,83\end{array}$ |

It can be seen from the data of Table 1 that the ratio $C_b^{\infty}/C_1^{\infty}$ decreases with increasing HClO₄ concentration. In H₂SO₄ solutions, the value of $C_b^{\infty}/C_1^{\infty}$ decreases the same as the activity of water K_{deh}(f_{i-C₅H₈/f_{ROH}) [8], and consequently, a_{H_2O} is not dependent on the acid concentration. In perchloric acid, K_{deh}(f_{i-C₅H₈/f_{ROH}) decreases with increasing HClO₄ concentration (Table 1). The values of this quantity were calculated by the use of the formula}}

$$K_{\text{deh}} \frac{f_{i-\text{C}_{\text{s}}\text{H}_{\text{s}}}}{f_{\text{ROH}}} = \frac{C_{\text{b}^{\infty}}}{C_{\text{i}}^{\infty}a_{\text{H}_{2}\text{O}}} \cdot \frac{1}{15.2}$$

As the standard state we selected 2.44% HC104, in solutions of which $K_{deh}(f_{i-C_{5}H_{B}}/f_{ROH}) = 15.2$.

On the basis of the experimental data, we consider that the detailed mechanisms of reaction (3) in H_2SO_4 and $HClO_4$ are identical. In $HClO_4$, the nucleophiles are H_2O molecules and ClO_4^- anions.

The influence of the medium on the effective rate constant in dehydration of an equilibrium mixture of DMVC and DMAA in HClO₄ is described by the equation

$$k_{\rm d} = k_{\rm d}^{\rm a} h_0 + k_{\rm d}^{\rm Nu} h_0 C_{\rm ClO_4}$$

In the derivation of this equation, it was assumed that the factors with the activity coefficients $f_{\rm ROH_4+}/f^*$ and $f_{\rm ROH_4+}f_{\rm GOA-}/f^*$ are independent of the acidity of the medium. Equation (4), the same as (1), is applicable under conditions such that the relative concentration of the protonated alcohol ${\rm ROH_2^+}$ can be neglected. The term $C_{\rm C10_4}$ - in Eq. (4) denotes the concentration of C10₄ anions, in moles/liter. It is known that in moderately concentrated aqueous solutions, HC10₄ is completely dissociated [11]; therefore, the value of $C_{\rm C10_4}$ - is equal to the analytically determined concentration of acid. We will invest Eq. (4) with the same meaning as Eq. (1). The symbols k_d^a and $k_d^{\rm Nu}$ denote the specific rate constants of dehydration through pathways α and b, respectively. The applicability of Eq. (4) in describing the influence of the medium on k_d is illustrated in Fig. 1. Specific rate constants were calculated by the use of Eq. (4) and the least squares method: $k_d^a = 7.2 \times 10^{-5} \pm 2.7 \times 10^{-5} \min^{-1}$; $k_d^{\rm Nu} = 7.7 \times 10^{-5} \pm 1.3 \times 10^{-5}$ liters/mole*min.

As can be seen from Table 1, $K_{deh}(f_{i-C_5H_8}/f_{ROH})$ varies with the concentration of HClO₄ in the solution. Therefore, in application to HClO₄ solutions, the influence of the medium on the rate constant for hydration of $i-C_5H_8$ can be expressed by the equation

$$k_{\rm h} = K_{\rm deh} \frac{f_{\rm i-C_{\rm s}H_{\rm s}}}{f_{\rm ROH}} \left(k_{\rm d}^{\rm a} a_{\rm H_{2}O} h_{\rm 0} + k_{\rm d}^{\rm Nu} a_{\rm H_{2}O} h_{\rm 0} C_{\rm ClO_{\rm s}^{-}} \right)$$
(5)

The data that we have obtained can also be described in a different way. If we assume, that in the acid, when the alcohol is ionized, a complex with an ion pair $H_3O^+ \cdot A^-$ is formed $(H_3O^+ \circ ClO_4^-)$ in the case of $HClO_4$ and $H_3O^+ \cdot HSO_4^-)$ in the case of H_2SO_4) and the ratio of concentrations of the ionized form (ROH $\cdot H_3O^+ \cdot A^-$) to the un-ionized form (ROH) is determined by the activity of the ion pair $\alpha_{H_3O^+} \cdot A^-$, then the rate of the dehydration reaction along pathway b is determined by the equation

$$\frac{W_{\rm d}^{\rm Nu}}{C_{\rm ROH}} = k_{\rm d}^{\rm Nu} \frac{a^*}{f^*} = k_{\rm d}^{\rm Nu} \frac{a_{\rm (ROH+H_sO+A^-)}}{C_{\rm ROH}f^*} =$$

$$= k_{\rm d}^{\rm Nu} \frac{C_{\rm (ROH+H_sO+A^-)}}{C_{\rm ROH}} \cdot \frac{f_{\rm (ROH+H_sO+A^-)}}{f^*} = \frac{k_{\rm d}^{\rm Nu}}{K_{\rm i}'} a_{\rm (H_sO+A^-)} \frac{f_{\rm (ROH+H_sO+A^-)}}{f^*} =$$
(6)

where

$$K_{i} = \frac{C_{\text{ROH}}a_{(\text{H}_{s}\text{O}^{+}\cdot\text{A}^{-})}}{C_{(\text{ROH}\cdot\text{H}_{s}\text{O}^{+}\cdot\text{A}^{-})}} \frac{f_{\text{ROH}}}{f_{(\text{ROH}\cdot\text{H}_{s}\text{O}^{+}\cdot\text{A}^{-})}} = \frac{C_{\text{ROH}}a_{\text{H}_{s}\text{O}}a_{\text{H}A}}{C_{(\text{ROH}\cdot\text{H}_{s}\text{O}^{+}\cdot\text{A}^{-})}} \frac{f_{\text{ROH}}}{f_{(\text{ROH}\cdot\text{H}_{s}\text{O}^{+}\cdot\text{A}^{-})}}$$
$$K_{i}' = K_{i} \frac{f_{(\text{ROH}\cdot\text{H}_{s}\text{O}^{+}\cdot\text{A}^{-})}}{f_{\text{ROH}}}$$

In the derivation of Eq. (6), it was assumed that the degree of ionization of the alcohol is small and that the factors $f_{(\text{ROH} \cdot \text{H}_{s}\text{O}^+ \cdot \text{A}^-)}/f^*$ and $f_{\text{ROH}}/f_{(\text{ROH} \cdot \text{H}_{s}\text{O}^+ \cdot \text{A}^-)}$ do not depend on the acidity of the medium. The effective rate constant for dehydration with the participation of the nucleophile is expressed by the equation

$$(k_{\rm ef}^{\rm Nu})_{\rm d} = (k_{\rm d}^{\rm Nu})' a_{\rm HA} a_{\rm HzO}$$
⁽⁷⁾

and the effective rate constant for dehydration varies in accordance with the equation

$$k_{\rm d} = k_{\rm d}^{\rm a} h_0 + (k_{\rm d}^{\rm Nu})' a_{\rm HA} a_{\rm HzO}$$

$$(k_{\rm d}^{\rm Nu})' = k_{\rm d}^{\rm Nu} / K_{\rm i}'$$
(8)

Equation (8) gives a satisfactory description of the influence of the medium in k_d in the experiments with HClO₄. This is illustrated in Fig. 1, where the data plot as a straight line on coordinates of k_d/h_0 vs $a_{\rm HClO_4}a_{\rm H,O}/h_0$.

The influence of the medium on k_h is described by the equation

$$k_{\rm h} = [k_{\rm h}^{\rm a} h_0 a_{\rm H_2O} + (k_{\rm h}^{\rm Nu}) a_{\rm HA} a_{\rm H_2O}^2] K_{\rm deh} \frac{f_{i-\rm C_8H_8}}{f_{\rm ROH}}$$
(9)

By application of the least squares method to Eq. (8), we obtain

$$k_{d}a = 9.1 \cdot 10^{-5} \pm 2.9 \cdot 10^{-5} \text{ min}^{-1}$$
$$(k_{d}^{Nu})' = 1.44 \cdot 10^{-4} \pm 0.2 \cdot 10^{-4} \text{ min}^{-1}$$

We will regard the ion pair $H_3O^+ \cdot A^-$ as a complex with a strong hydrogen bond, and we will ascribe to this complex the structure



The limiting stage of the DMVC dehydration reaction along pathway b can be represented as



Equation (8) also describes the data from the experiments with H_2SO_4 solutions that were reported in [8] (Fig. 2). From calculations based on Eq. (8), it is found that for H_2SO_4 solutions at 25°C,

$$k_{\rm d}^{\rm a} = 8.3 \cdot 10^{-5} \pm 2.4 \cdot 10^{-5} \text{ min}^{-1}$$

 $(k_{\rm d}^{\rm Nu})' = 9.7 \cdot 10^{-3} \pm 2.7 \cdot 10^{-3} \text{ min}^{-1}$



Fig. 1. Illustration of applicability of Eqs. (4) and (8) in describing the influence of the medium on rate constants for dehydration of DMVC-DMAA mixture to isoprene: 1) calculation according to Eq. (1); 2) calculation according to Eq. (4).

Fig. 2. Dependence of k_d/h_0 on ${}^a_{H_2SO_4}{}^a_{H_1O}/h_0$ for dehydration of equilibrium mixture of alcohols to isoprene in aqueous H_2SO_4 solutions at 25°C.

At the present time, owing to the insufficient amount of experimental data, we cannot make a choice between Eqs. (4) and (8) or between (5) and (9).

In the calculations, we used values of h_o from [12] and $a_{\rm H_2O}$ from [13]. The values of $a_{\rm HC1O_4}$ and $a_{\rm H_2SO_4}$ were calculated in the basis of the mean ion activity coefficient taken from [14].

SUMMARY

1. A study has been made of the kinetic relationships in the formation of isoprene from an equilibrium mixture of 3-methyl-1-buten-3-ol and 3-methyl-2-buten-1-ol in aqueous perchloric acid solutions with concentrations from 2.44% to 29.95% by weight, at 25°C.

2. The Cl04 anions act as a nucleophile in promoting these reactions.

3. In the dehydration of isoamylene alcohols to isoprene, the catalytic effect of perchloric acid is manifested not only in protonation of the alcohol, but also in nucleophilic catalysis by the ClO₄ anion.

4. Equations have been derived to describe the influence of the medium on the effective rate constants in the dehydration of unsaturated alcohols and the hydration of isoprene; rate constants characterizing the catalytic effect of the medium have been calculated.

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QUENCHING OF DUROQUINONE BY AROMATIC DONORS OF ELECTRON AND

HYDROGEN ATOM

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Triplet states of quinones react with electron donors through a charge transfer mechanism; the reaction rate constant increases with decreasing ionization potential of the donor [1, 2]. As a result of quenching by aromatic electron donors in low-polarity solvents, short-lived triplet exciplexes are formed [3, 4]. The structure of such exciplexes depends on the donoracceptor properties of the reactants and on the solvating power of the medium. The contribution of the state with complete charge transfer (CCT) to the structure of the triplet exciplexes will increase with increasing reduction potential of the quinone and with decreasing oxidation potential of the electron donor; the contribution also increases upon solvation by alcohols [5, 6]. In low-polarity solvents, the destruction of triplet exciplexes is accomplished through a mechanism of radiationless intercombination conversion to the ground state [3, 4]; the rate constant for this process increases with decreasing energy level of the triplet exciplex [6, 7]. With an increase in the dielectric constant of the medium, there is now a second channel for destruction of the triplet exciplexes, i.e., dissociation into ion-radicals [5, 7]. The rate constant for dissociation of polar triplet exciplexes into ion-radicals is well described by the theory of diffusion-controlled dissociation of ion pairs in liquid solutions [5, 7, 8].

Triplet states of quinones will abstract a H atom from aromatic compounds containing N-H or O-H groups [3, 9, 10-12]. In the case of secondary aromatic amines, the transfer of the H atom takes place in a collision complex, and it competes with electron transfer [3, 9]. The outcome of the competition between these two reactions will depend on both the donoracceptor and acid-base properties of the reactants [10]. The transfer of a H atom is apparently accomplished by establishing an acid-base equilibrium in the radical pair formed after electron transfer, the same as in quenching by tertiary amines [13].

The kinetics and mechanism of photoreduction of quinones by aromatic donors of an electron and an H atom are also determined by the structure and kinetics of the destruction of the triplet exciplexes that are formed; however, the interrelation among the kinetics of triplet quenching, the nature of the radicals that are formed, and the properties of the exciplexes have not been investigated adequately.

In the present work, we applied pulse photolysis in a kinetic study of quenching of the triplet state of duroquinone by aromatic donors of an electron and an H atom in various solvents; we also investigated the nature of the intermediate species formed in the quenching. This quinone is of special interest, since it is the simplest model of quinones that are of biological importance.

EXPERIMENTAL

The absorption spectra and kinetics of the destruction of the intermediate products were investigated by means of a pulse photolysis unit [14]. The solutions were photoexcited by radiation in the 370-450 nm region. The solutions were pumped down to 10^{-4} torr to remove O_2 . All measurements were performed at 20 ± 1°C. The duroquinone (DQ) and the donors of the H atom (RH) were as follows: N,N-dimethyl-4-methoxyaniline (I); N,N-dimethylaniline (II);

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