double salt also forms solid solutions. Although the internal structure of $Li_2SO_4 \cdot H_2O$ has been determined,[22] it is unfortunate that the structure of $LiNH_4SO_4$ has not. It would be interesting to see whether the role of NH_4^+ ion in $LiNH_4SO_4$ is the same as that of the combination Li^+–H_2O in $Li_2SO_4 \cdot H_2O$.

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COMMUNICATIONS TO THE EDITOR

MECHANISM OF THE REACTION OF NITROMETHANE WITH BASES

Sir:

We wish to report a mechanism for the reaction of nitromethane with bases in aqueous solutions which accounts for both the initial reaction to form the salt of the aci form of nitromethane, and the subsequent slower reaction to form the salt of methazonic acid.

$$CH_3NO_2 + OH^- \rightleftharpoons CH_2NO_2^- + H_2O \quad (1)$$

$$2\ CH_2NO_2^- \xrightarrow{k_2} O_2NCH_2CHNO^- + OH^- \quad (2)$$

We have found that basic solutions containing methazonate ion show very strong absorption of light at 2,980 Å. while acid solutions show none. We have also observed that freshly prepared mixtures of dilute solutions of nitromethane and bases react at relatively slow rates to form the methazonate ion which we can follow by observing the increasing absorption at 2,980 Å. with time. The identification of the absorption peak with the methazonate ion has been made by preparing ammonium methazonate by a well established procedure (3) and establishing the absorption spectra pattern of this material.[8]

Our studies at 25.6° show that the initial rate of formation of methazonate ion is second order with respect to the initial concentration of nitromethane over the range of *p*H from 9.5 to 12.5. The order with respect to hydroxide ion concentration is second order at *p*H 9.5, and decreases asymptotically to almost zero order as we increase the *p*H to 12.5. It should be noted that the *p*H remains constant during the course of any single experiment.

On the assumption that the equilibrium in reaction (1) is established very rapidly relative to the velocity of reaction (2), an expression can be derived for the over-all rate from equations (1) and (2) as shown

$$r = \frac{k_2 K^2 X^2 (OH^-)^2}{[1 + K(OH^-)]^2} \quad (3)$$

where

r = rate of formation of methazonate ion
k_2 = specific rate constant for reaction (2)
K = equilibrium constant for reaction (1)
X = concentration of nitromethane plus aci nitromethane.

The kinetic data obtained are in complete agreement with equation (3).

This relation enables us to estimate K at higher temperatures than has been heretofore possible, and we will also be able to obtain the ΔH for reaction (1) and the activation energy for reaction (2). It should be noted that the evaluation of K is not our primary purpose. Rather we wish to show that known values of K_N are entirely consistent with our proposed mechanism.

This work supports the Pedersen mechanism[1] for pseudo acid behavior of nitro paraffins and gives good agreement with published data[2,3] on the ionization constant of nitromethane, K_N. This constant is related through the water equilibrium constant K_W to our equilibrium constant K in the following way

$$K = K_N/K_W$$

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CARBON DIOXIDE FIXATION IN HEART EXTRACTS BY β-HYDROXYISOVALERYL COENZYME A[1]

Sir:

Previous isotopic studies have indicated that isovaleric acid, an intermediate in leucine metabolism, yields acetoacetate in liver tissue.[2,3,4,5,6] Carbons 1 and 2 furnish "acetate" for the well-recognized acetoacetate condensation, and the carbons of the isopropyl group yield acetoacetate by a carbon dioxide-fixing reaction. The intermediate steps in this metabolic pathway have recently been investigated in heart and liver extracts in this laboratory, and the following series of reactions is proposed to account for the results obtained

$$\text{Isovaleryl CoA} \longrightarrow \text{Senecioyl CoA}^7 \quad (1)$$

$$\text{Senecioyl CoA} + H_2O \longrightarrow \text{HIV CoA} \quad (2)$$

$$\text{HIV CoA} + CO_2 \xrightarrow{\text{ATP}} \text{HMG CoA} \quad (3)$$

$$\text{HMG CoA} \longrightarrow \text{Acetoacetate} + \text{Acetyl CoA} \quad (4)$$

(1) Supported by grants from the National Science Foundation and the United States Public Health Service.
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(7) Abbreviations: acyl Coenzyme A derivatives, acyl CoA; β-hydroxyisovaleryl CoA, HIV CoA; β-hydroxy-β-methylglutaryl CoA, HMG CoA; adenosine triphosphate, ATP; tris-(hydroxymethyl)-aminomethane, Tris.