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KINETIC STUDIES ON FAST REACTIONS IN SOLUTION

I. Photoreduction of 2-Acetonaphthone

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The photoreduction of 2-acetonaphthone by $(\text{Bu})_3\text{SnH}$ and $(\text{Bu})_3\text{SiH}$ were investigated by the method of flash photolysis and compared with the results obtained from the steady state method. The rate constant of the reduction by $(\text{Bu})_3\text{SnH}$ was found to be $1.3 \times 10^6 \text{ l mole}^{-1} \text{ sec}^{-1}$, which is close to that of Linschitz *et al.* The temperature dependence of the rate constant gives the activation energy of $1.7 \text{ kcal mole}^{-1}$.

The reduction by $(\text{Bu})_3\text{SiH}$ was found not to occur even after a long exposure to sunlight. Furthermore we discuss qualitatively about the activation energy and the reactivity of reducing agents.

Introduction

As the photoreductions of ketones have long been much interested^{1,2)} and investigated quite well, there are many informations about their reaction mechanism.³⁾⁻¹⁰⁾ Alkyl ketones usually have $(n\pi^*)$ states as their lowest excited states, but aromatic ketones have $(n\pi^*)$ or $(\pi\pi^*)$ states according to the kind of substrates they have. This change of the excited states of aromatic ketones causes characteristic variations of the reactivity.

In the $(n\pi^*)$ state, one electron of n -orbital of oxygen delocalizes over the whole π -system, and therefore the oxygen atom becomes electropositive. On the other hand, when a molecule is excited to the $(\pi\pi^*)$ state, the charges move to the oxygen atom,¹¹⁾ so it becomes electronegative (or we can explain as follows¹²⁾: the hydrogen abstraction reaction by the triplet benzophenone is quite analogous to that of the *t*-butoxy radical, so that the $(n\pi^*)$ state, different from the $(\pi\pi^*)$ state, has a radical-like character.). Therefore, the molecules which have $(n\pi^*)$ states in their lowest triplets are more easily

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reduced than those which have the ($\pi\pi^*$) states. For example, benzophenone, which has the ($n\pi^*$) state in its lowest triplet, is photoreduced by alcohol, but acetophenone, which has the ($\pi\pi^*$) state in its lowest triplet, can not be photoreduced by alcohol. However, if we use strong reducing agents such as $(\text{Bu})_3\text{SnH}$, it is known that ketones which have the ($\pi\pi^*$) states can be photoreduced.

The present paper deals with the photoreduction of 2-acetophenone by $(\text{Bu})_3\text{SnH}$ and $(\text{Bu})_3\text{SiH}$. The relations between the properties of the excited states and bond energies of reducing agents have not been studied thoroughly so far. It will, therefore, be very interesting to study the photoreductions of ketones by using various reducing agents with different bond energies or by reducing different ketones by the same reducing agent. We will report them later.

Experimentals

Apparatus

Our apparatus is not so different from the ordinary flash photolysis equipments, but as this is our first report on the flash photolysis, it will be convenient to describe our apparatus in detail.

The block diagram of our apparatus for the spectrophotometric method is shown in Fig. 1 and the discharging circuit in Fig. 2. A tungsten lamp operated by batteries is used as a source of monitoring beam. The flash tube is a cylindrical one devised by Hardwick *et al.*¹³⁾ and made of quartz and filled with argon gas up to pressures of 15–18 cmHg. Half life of the flash duration is about 10 μsec and its out-put energy is about 100 joules. The reaction vessel made of pyrex is 15 cm long and has a side arm to degas. The changes in T-T' absorption with time are recorded by a synchroscope equipped with a polaroid camera.

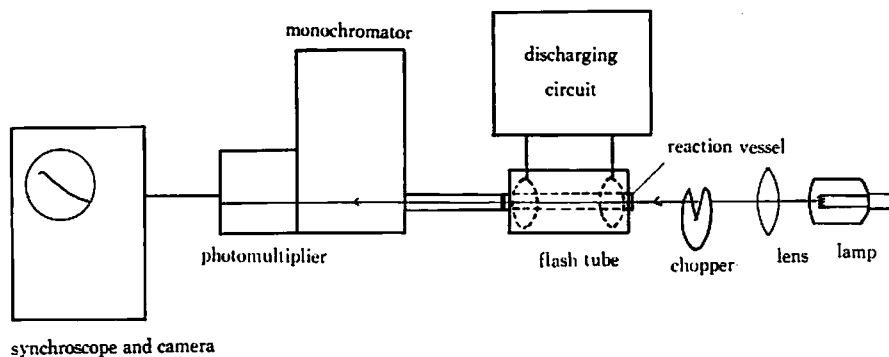


Fig. 1 Block diagram of our apparatus

Material

2-acetophenone: 2-acetophenone commercially available (G. R. grade) was recrystallized from spectro-grade benzene.

$(\text{Bu})_3\text{SnH}$ (tri-*n*-butylstannane): By the method of van der Kerk,¹⁴⁾ $(\text{Bu})_3\text{SnH}$ was synthesized from $(\text{Bu})_3\text{SnCl}$ by reduction with LiAlH_4 and purified by distillation. On account of its instability

13) R. J. Charlson, H. Harrison and R. Hardwick, *Rev. Sci. Instr.*, **31**, 46 (1960)

14) G. J. M. van der Kerk, J. G. Noltes and J. G. A. Luijten, *J. Appl. Chem.*, **7**, 366 (1957)

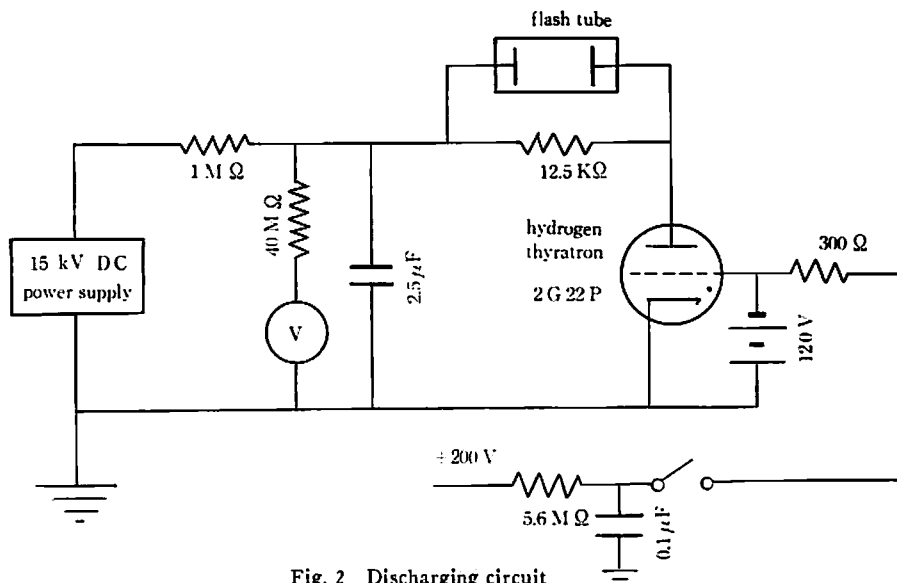


Fig. 2 Discharging circuit

in the air, it was stored in the degassed capsule placed in the dark. Its benzene solution was also kept in the dark, and we did not use the sample which had passed long time after preparation.

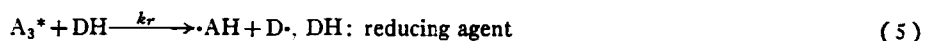
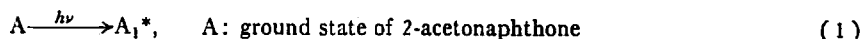
(Bu)₃SiH (tri-*n*-butylsilane): This was synthesized from trichlorosilane and *n*-butylmagnesium bromide and purified by distillation.¹⁵⁾ This is stable in the air.

In all runs we used spectro-grade benzene as the solvent. The concentration of 2-acetonaphthone was *ca.* 5×10^{-4} mole/l. The sample was made in a dark room by mixing this solution with a relevant amount of (Bu)₃SnH or (Bu)₃SiH dissolved in spectro-grade benzene and degassed by repeating a freeze-pump-thaw cycle six times.

To avoid the changes in the concentration of reactants due to several flashes, the T-T' absorption changes were recorded at the first or the second flash alone.

Results

The reaction mechanisms are probably as follows,



15) H. Gilman, D. H. Miles, L. O. Moore and C. W. Gerow, *J. Org. Chem.*, **24**, 219 (1959)



The steps (1), (2), (3) and (4) are nothing but usual excitation and deactivation processes, so there is no need to state furthermore about them. The step (5) is proposed by the analogy of the photoreduction of ketones by alcohols and more firmly by our result (see Fig. 5). The processes (6) and (7) may be considered appropriate from the facts that the corresponding pinacol is not detected, and that the tin monohydride compounds do not form cross-coupled products but do ditin when they are used as reducing agents for several alkyl or aromatic ketones.¹⁶⁾ However, the process which we are particularly interested in is (5), and therefore we will not discuss about the other steps any more.

Next we will state how to determine k_r .

Reduction by $(Bu)_3SnH$

The triplet state molecule of 2-acetonaphthone has the T-T' absorption maximum at 435 m μ .¹⁷⁾ The relative changes in the concentration of the triplet state molecules are measured from the changes in the absorption intensity at this wave length. In the absence of the reducing agent, it

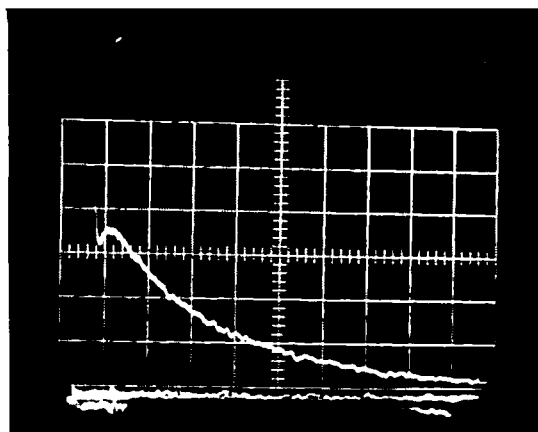


Fig. 3 Decay curve of the T-T' absorption of 2-acetonaphthone in the absence of the reducing agent. One larger division designates 50 μ sec.

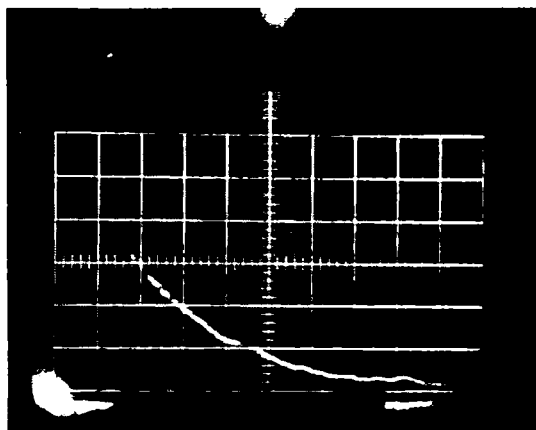


Fig. 4 Decay curve of the T-T' absorption of 2-acetonaphthone in the presence of $(Bu)_3SnH$ 1.0×10^{-2} mole/l. One larger division designates 20 μ sec.

16) H. G. Kuivila and F. Beumel, Jr., *J. Am. Chem. Soc.*, **83**, 1246 (1960)

17) W. A. Bryce and C. H. J. Wells, *Can. J. Chem.*, **41**, 2722 (1963)

obeys the first order rate equation (8),

$$\frac{d[A_3^*]}{dt} = -k_t[A_3^*] \quad (8)$$

Assuming Beer's law at the wave length, $k_t = 9.8 \times 10^3 \text{ sec}^{-1}$ is obtained by the analysis of Fig. 3. In the presence of the reducing agent, if we represent the rate constant of the decay of A_3^* by k , equation (9) can be obtained.

$$\frac{d[A_3^*]}{dt} = -k[A_3^*] = -\{k_t + k_r[DH]\}[A_3^*] \quad (9)$$

Using the equation, the apparent rate constant k can be estimated similarly as in eq. (8). Fig. 5 gives a plot of $(k - k_t)$ vs. $[DH]$. From this straight line it is obvious that the reduction of A_3^* by DH is first order with respect to $[A_3^*]$ and $[DH]$, and we obtain $k_r = 1.3 \times 10^6 \text{ l mole}^{-1} \text{ sec}^{-1}$ as the reduction rate constant. To make it clear whether A_3^* is deactivated by other processes of $(\text{Bu})_3\text{SnH}$ than the reduction or not, we used the same amount of $(\text{Bu})_4\text{Sn}$ instead of $(\text{Bu})_3\text{SnH}$. In this case the decay rate $k[A_3^*]$ was not accelerated compared with the decay rate in the absence of the reducing agent. Then we can conclude that the k_r obtained above is the true reduction rate constant.

To determine the activation energy of the process (5), we measured k_r at 10°C , 25°C and 40°C . The Arrhenius plot of the result is shown in Fig. 6. The slope gives the activation energy $1.7 \text{ kcal mole}^{-1}$, the error of which is within 10%.

When the degassed sample was exposed to sunlight, 2-acetonaphthone was reduced rather rapidly and after twenty or thirty minutes, its T-T' absorption disappeared.

Reduction by $(\text{Bu})_3\text{SiH}$

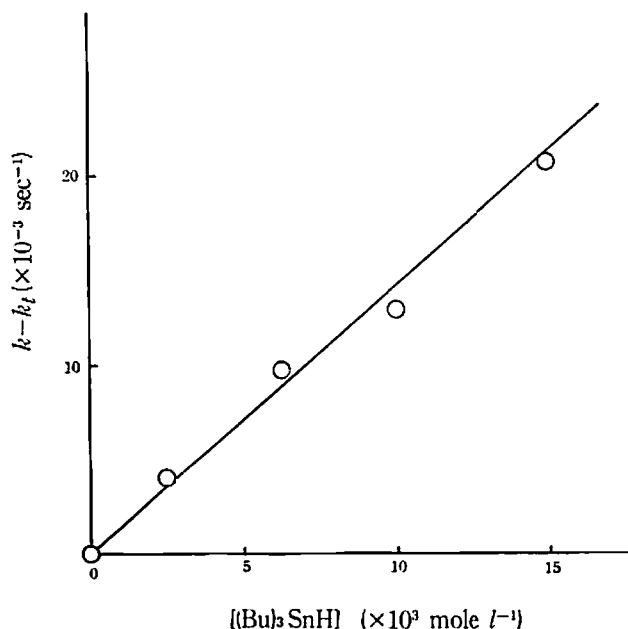
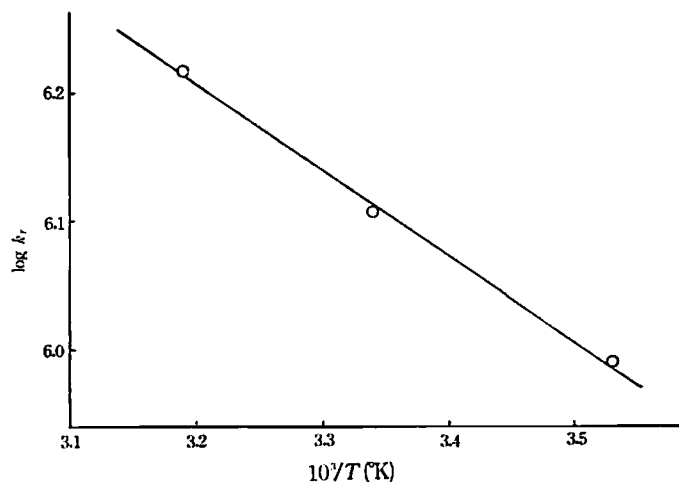


Fig. 5 The plot of $k - k_t$ vs. $[DH]$

Fig. 6 Arrhenius plot of k_r

We did the same experiments with $(\text{Bu})_3\text{SiH}$ as with $(\text{Bu})_3\text{SnH}$ (but in this case we used $(\text{Bu})_3\text{SiH}$ solution 10 times as concentrated as in the case of $(\text{Bu})_3\text{SnH}$), but 2-acetonaphthone was not reduced and even when it was exposed to sunlight for several days, its T-T' absorption was unchanged.

Discussion

The other method to determine k_r

We determined k_r directly by the method of flash photolysis, but G. S. Hammond *et al.* used another method to obtain k_r . The following equation gives the quantum yield of photoreduction Φ ,

$$\frac{1}{\Phi} = \frac{1}{\Phi'} + \frac{k_d}{\Phi' k_r [\text{DH}]} + \frac{k_q [\text{Q}]}{\Phi' k_r [\text{DH}]}$$

where

Q: quencher

Φ' : intersystem crossing quantum yield

k_d : decay rate constant of the triplet state

k_q : quenching rate constant of the triplet state.

Assuming that k_q is equal to the diffusion-controlled rate constant $2 \times 10^9 \text{ l mole}^{-1} \text{ sec}^{-1}$ for ferric dipivaloyl methide in the equation above, they found $k_r = 2 \times 10^6 \text{ l mole}^{-1} \text{ sec}^{-1}$. On the other hand, H. Linschitz *et al.* determined k_q directly by the method of flash photolysis and from this and Hammond's results, they obtained $k_r = 0.9 \times 10^6 \text{ l mole}^{-1} \text{ sec}^{-1}$. Our value is close to that of Linschitz, and a little different from Hammond's value based on the assumption about k_q .

Activation energy

As we can assume an activated complex for the reaction in the ground state, we shall also be able to do some activated complex for the reaction in the excited state. If a reactant in the excited state has a suitable configuration to form the activated complex, or enough energy to compose the activated complex, the activation energy is naturally supposed to be small, and might be smaller

than that of diffusion in some cases. Though we can not make a discussion in detail by the lack of data on the activation energies of photoreduction of ketones, the measured activation energy will possibly be that of diffusion. To explain k_r reasonably for the activation energy, we must consider the steric factor of the order 10^{-3} . This figure will not be too small, taking account of the three comparatively large butyl groups.

Difference between $(\text{Bu})_3\text{SnH}$ and $(\text{Bu})_3\text{SiH}$

Bond energies of the reducing agents are thought to play a dominant role in this photoreduction. $(\text{Bu})_3\text{SnH}$ and $(\text{Bu})_3\text{SiH}$ have I. R. absorptions which result from the stretching mode of $\text{Sn}-\text{H}$ or $\text{Si}-\text{H}$ at $1,820\text{ cm}^{-1}$ and $2,108\text{ cm}^{-1}$, respectively.¹⁸⁾⁻²⁰⁾ The reason why $(\text{Bu})_3\text{SiH}$ did not react could be attributed to the larger bond energy. ($(\text{Bu})_3\text{SiH}$ can reduce benzophenone.) To make it sure, it will be quite interesting to investigate the photoreduction of 2-acetonaphthone by $(\text{Bu})_3\text{GeH}$ which may have the intermediate bond energy.

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