Photoinduced Anthrone to Anthranol Isomerization in Ethyl Ether

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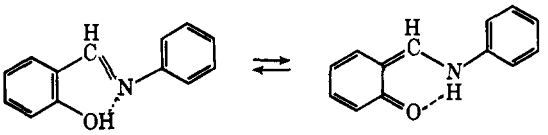
Abstract: Mainly by means of the flash spectroscopy technique, the mechanism of photoinduced anthrone → anthranol isomerization in ethyl ether was studied. The anthrone ketyl radical was found spectroscopically as a reactive intermediate. From the analysis of the decay curve of the radical and also from the identification of the reaction products, the following reaction mechanism and rate constants were finally obtained: anthrone (+ $h\nu$) → anthrone* (triplet); anthrone* (triplet) + ethyl ether → anthrone ketyl radical + 1-ethoxyethyl radical; 2(anthrone ketyl radical) → anthrapinacol ($k = 7\ (\pm 1) \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$); anthrone ketyl radical + 1-ethoxyethyl radical → anthranol + ethyl ether ($k = 4\ (\pm 1) \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$); 2(1-ethoxyethyl radical) → 2,3-diethoxybutane.

Photoinduced isomerization reactions accompanying proton transfer are an interesting research subject. The photoinduced proton transfer of various compounds, for example



has been studied extensively by several authors[1] in connection with the mechanism of photochromy. In particular, the development of the flash spectroscopy technique greatly facilitated the progress of research in this kind of reaction. For instance, Wettermark[2] studied the photoinduced isomerization of *o*-nitrotoluene with the aid of this technique and found $H_2CC_6H_4NO_2H$ as the short-lived isomer. Generally speaking, however, the detailed mechanism of photoinduced proton-transfer reaction remains unsolved.

Anthrone and anthranol is a typical example of the keto–enol isomerization in solution. Baba and Takemura studied the thermal isomerization of anthrone and found that a third substance such as amine accelerates the reaction rate and changes the equilibrium constant.[3] We have studied the photoinduced isomerization of anthrone to anthranol and have succeeded in finding the reaction intermediate in ethereal solution by the aid of the flash spectroscopy technique and in clarifying the reaction mechanism.[4]

Experimental Section

Materials. Anthrapinacol was synthesized from anthrone by the aid of the Clemmensen reduction[5] method and was recrystallized twice from ethanol, mp 180°. Dianthranol obtained as a main product in the experiment of steady-light illumination of anthrone was washed by ethyl ether and thereafter was recrystallized twice from ethanol. The white crystals obtained decomposed at ~200° with sublimation. Commercially available anthrone (GR grade of Tokyo Kasei) was used without further purification, because it was converted to some extent into anthranol in usual solvents and its purity could hardly be improved upon by recrystallization from them. Its purity was certified from its melting point (156°) and the uv spectrum. Ethyl ether, ethanol, and *n*-heptane used as solvents were purified by the usual methods.[6,7] Acetonitrile was purified by the method described previously.[8] The purity of the solvents was checked by observing uv spectra.

Apparatus and Measurement. Two quartz flash lamps filled with argon were used for the photoinduced isomerization. The input energy was varied from 300 to 700 J by changing the applied voltage in the range of 8–12 kV with the capacitance of 10 μF. A spectroflash was operated at 6 kV and 5 μF. The half-width of the duration time curve was about 10 and 5 μsec for the main flash and the spectroflash, respectively. The time interval between the former and the latter was controlled through a delay circuit.

Absorption spectra were taken with a Hilger Type E_2 quartz spectrograph by using Fuji Neopan films. For measuring the decay of transient absorption, the sample was monitored by a tungsten lamp (10 V, 4 A) or by a xenon lamp (Ushio 500 W) with a Type 1P28 photomultiplier as a detecter attached behind an exit slit of the spectrograph. The signal was recorded with a synchroscope (Iwasaki SS-5302) through a dc amplifier.

Quartz reaction cells 10 cm long and 20 or 12 mm in diameter were used. The solution was degassed by repeating freezing, evacuation, and dissolution and further by vacuum distillation. Particularly, ethyl ether as a solvent was transferred from a reservoir containing the solvent with sodium metal to the reaction vessel containing solute (anthrone) within the same vacuum line system after degassing.

The uv absorption spectra of stable specimens under usual conditions were measured by a Cary recording spectrophotometer Model 14. Ir and nmr spectra were measured by a Hitachi Type EPI-2 spectrophotometer and by a Japan Electron Optics Type JNN-3H-60 spectrometer, respectively. A Shimazu Type 1D gas chromatography apparatus was used for the determination of reaction products.

Results and Discussion

Finding of Reaction Intermediate. The absorption spectrum of degassed ethereal solution of anthrone was measured before and after a flash irradiation with the results given in Figure 1. Curve 1 in this figure corresponding to anthrone changes to curve 3 due to anthranol after the irradiation. This means that the flash irradiation easily changes the former to the latter. Further, we succeeded in observing a transient absorption spectrum due to a reaction intermediate by the flash spectroscopy technique. Curve 2 is a microphotometer tracing curve of the transient absorption in the region

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[1] E. Fischer, *Fortschr. Chem. Forsch.*, **7**, 605 (1967).

[2] G. Wettermark, *Nature*, **194**, 677 (1962).

[3] H. Baba and K. Takemura, *Bull. Chem. Soc. Japan*, **37**, 1241 (1964).

[4] A preliminary result of this work was published in the following short communication: N. Kanamaru and S. Nagakura, *ibid.*, **39**, 1355 (1966).

[5] H. L. Bradlow and C. A. VanderWerf, *J. Am. Chem. Soc.*, **69**, 1254 (1947).

[6] A. Weissberger and E. S. Proskauer, "Technique of Organic Chemistry, Vol. VII, Organic Solvent," Interscience Publishers, New York, N. Y., 1935.

[7] H. Yada, J. Tanaka, and S. Nagakura, *Bull. Chem. Soc. Japan*, **33**, 1660 (1960).

[8] Y. Bando and S. Nagakura, *Theoret. Chim. Acta*, **9**, 210 (1968).

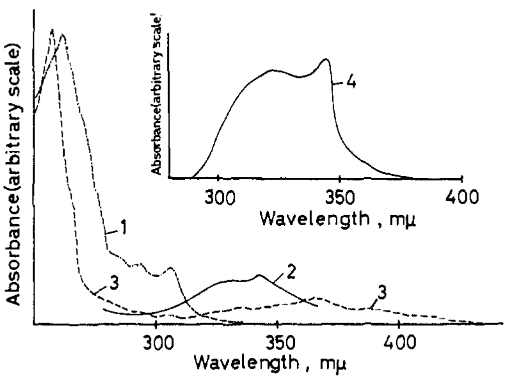

Figure 1. Absorption spectra (curves 1–3) of the ethereal solution of anthrone under various conditions and the absorption spectrum (curve 4) of the benzophenone ketyl radical: (1) before irradiation, (2) immediately (25 μsec) after irradiation, (3) (a few minutes) after irradiation, (4) benzophenone ketyl radical (by Porter and Wilkinson[9]).

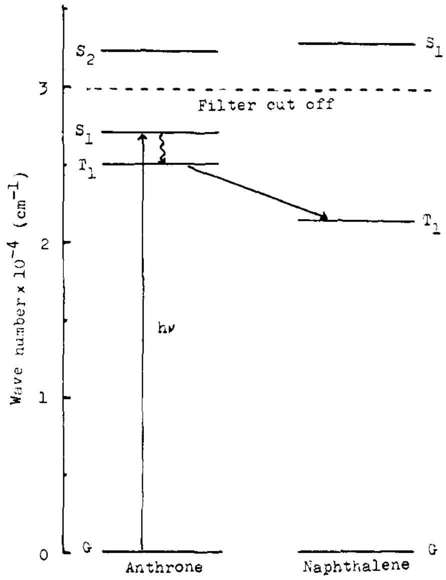

Figure 2. Energy-level diagram of anthrone and naphthalene.

of 280–370 mμ and is assigned to the anthrone ketyl radical from its resemblance in position and shape to the absorption spectrum of the benzophenone ketyl radical, observed by Porter and Wilkinson;[9] it is also shown in Figure 1 (curve 4) for the purpose of comparison. We observed another transient absorption band at ~550 mμ for the irradiated anthrone, though it is not shown in Figure 1, as in the case of the benzophenone ketyl radical. It is reasonable that the absorption spectra of these two radicals are similar to each other, in view of the similarity in their π-electron structures.

The formation of the ketyl radical as one of the steps of the photoinduced anthrone → anthranol isomerization is also supported by the experiment on the solvent effect. In *n*-heptane and acetonitrile, the yield of anthranol was very small (at most a few per cent for one flashing). On the other hand, in ethanol and ethyl ether which are known to have "active hydrogen," the photoinduced isomerization was found to occur easily. This solvent dependence supports the view that the ketyl radical produced through the abstraction of hydrogen by excited anthrone from solvent is the intermediate in the anthrone → anthranol reaction.

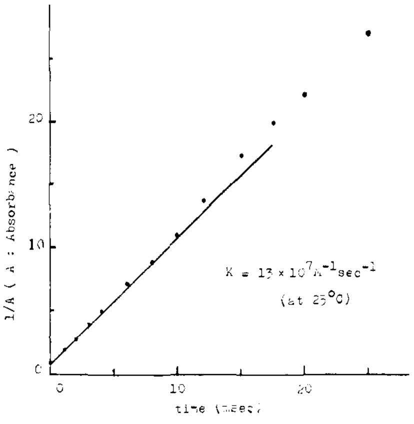

Figure 3. Application of the second-order reaction formula for the ketyl radical disappearance.

Porter and Wilkinson[9] showed that the formation of benzophenone ketyl radical proceeds through the n,π* triplet state. The same may be the case for the formation of the anthrone ketyl radical. In order to make it certain, we made experimental works concerning the effect of oxygen and other triplet energy quenchers upon the reaction. The sample exposed to air did not show the above reaction, that is to say, the formation of the anthrone ketyl radical seems to be prohibited by oxygen. Furthermore, by the addition of 10^{-2} *M* naphthalene or biphenyl the reaction was inhibited. This phenomenon is schematically explained in Figure 2 for the case of naphthalene with the aid of the energy levels of anthrone given by Shimada and Goodman.[10] Anthrone is excited to its lowest singlet excited state by light illumination, and thereafter the excitation energy can be transferred efficiently by the intersystem crossing to the lowest (n,π*) triplet state in which the hydrogen abstraction can occur. Under the coexistence with naphthalene or biphenyl, however, the triplet excited state can be expected to be easily quenched by them,[11] because their lowest triplet state is lower than that of anthrone as is shown in Figure 2. In this connection, it should be added that the reaction was not prohibited by the addition of benzene (~1 *M*), the lowest triplet state of which lies higher than that of anthrone.

The Decay of the Ketyl Radical. The decay of the ketyl radical produced by flash irradiation was studied by measuring photoelectrically the time dependence of the absorption intensity (*A*) at 340 mμ. The measurement was made for the solutions of various concentrations ranging from 10^{-5} to 10^{-4} *M* at 25°. As an example, the decay curve observed for the 1.5 × 10^{-5} *M* solution is shown in Figures 3 and 4. The results show that the decay curve follows at the initial (first) stage the second-order reaction formula and at the second stage the first-order one. In Figure 3, the observed 1/*A* values were plotted *vs.* times and a straight line was obtained for the initial stage of the reaction.

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[9] G. Porter and F. Wilkinson, *Trans. Faraday Soc.*, 57, 1686 (1961).

[10] R. Shimada and L. Goodman, *J. Chem. Phys.*, 43, 2027 (1965).

[11] The flash irradiation for the mixed solutions was made through a glass reaction vessel, and therefore the uv light necessary for the direct excitation of naphthalene and biphenyl to their singlet excited states seems to be almost completely cut off.

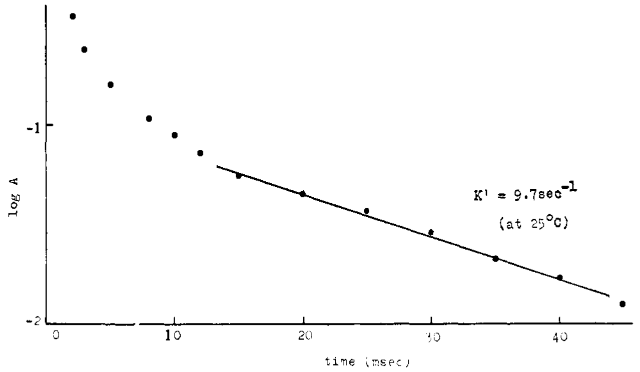

Figure 4. Application of the first-order reaction formula for the ketyl radical disappearance.

From its gradient the second-order rate constant K was found to be $13 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$ at 25° on the reasonable assumption that the initial concentration of the ketyl radical is the same as the difference in that of anthrone before and immediately after the irradiation.[12] As is seen in Figure 4 the plots of log A *vs.* time satisfies the straight-line relation at the second stage of reaction. The first-order rate constant for the solution with an initial anthrone concentration of $1.5 \times 10^{-5}\ M$ was found to be $9.7\ \mathrm{sec}^{-1}$ at 25° from its gradient. The value is dependent upon the initial concentration as is explained later in the present paper.

Determination of Reaction Products. We identified spectroscopically a typical product of this reaction as anthranol. We may expect the other possible reaction products such as anthrapinacol from the existence of the ketyl radical as a reactive intermediate. Since we could not identify them from the electronic absorption spectrum alone, chemical analysis and gas chromatography in addition to the other molecular spectroscopy techniques such as ir and nmr spectra were used for the identification and determination of the products. The experiments were carried out for the two cases of flash illumination and steady-light illumination.

First we explain the experimental result of flash-light illumination. The yield of anthranol by a flash irradiation was determined to be 40%[13] from the absorption intensity at 380 mμ. The other products could not be identified spectroscopically, because they did not show any characteristic band in the longer wavelength region than 260 mμ. Chemical separation of the products was unsuccessful because of a small concentration and of a small amount of solution. Only the ir data suggest the existence of anthrapinacol.

In order to accumulate the reaction products other than anthranol, flashing and boiling of the solution were alternatively repeated. This is based on the fact that anthranol converts into anthrone by boiling the solution on a water bath. The products were analyzed and identified by gas chromatography, and anthrapinacol was found to be the main product other than anthranol.[14]

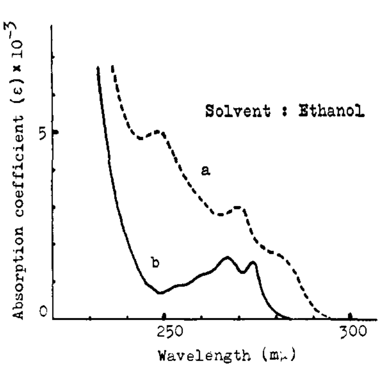

Figure 5. Uv spectra of dianthranol (curve a) and anthrapinacol (curve b).

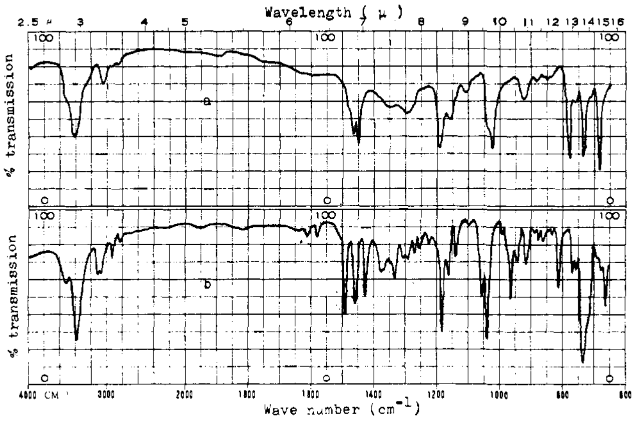

Figure 6. Ir spectrum of dianthranol (curve a) and anthrapinacol (curve b).

For the purpose of checking further the reaction products, we performed another experiment using steady-light illumination. The degassed $10^{-2}\ M$ ethereal solution of anthrone was illuminated by a 100-W high-pressure Hg lamp (Toshiba). In this case a main product identified as dianthranol precipitated during the reaction. Illumination was continued until the yellow color of anthranol almost completely disappeared. The precipitate produced by the illumination was filtered off, washed with ethyl ether, and purified by recrystallization from ethanol twice. An elementary analysis of the sample identified it as dianthranol. The uv, ir, and nmr spectra of the sample support this identification. The uv spectrum shown in Figure 5 resembles fairly well that of dianthracene. This is reasonable with regard to the structure of dianthranol. The ir spectrum of the sample (curve a in Figure 5) confirms the existence of $-$OH and $>$CH groups. The nmr spectrum of the sample in DMSO at 78° shows the existence of the phenyl ($\tau \sim 2.9$), $-$OH (τ 6.6), and $>$CH groups (τ 6.9). The yield of dianthranol was determined to be 70% by the aid of the gas chromatography technique with an internal reference.

Anthracene is known to be easily dimerized by uv light irradiation.[15] From an analogy with this, the formation of dianthranol can reasonably be explained by the photodimerization of anthranol.

The formation of anthrapinacol was confirmed by uv, ir, and nmr spectra and gas chromatography; the

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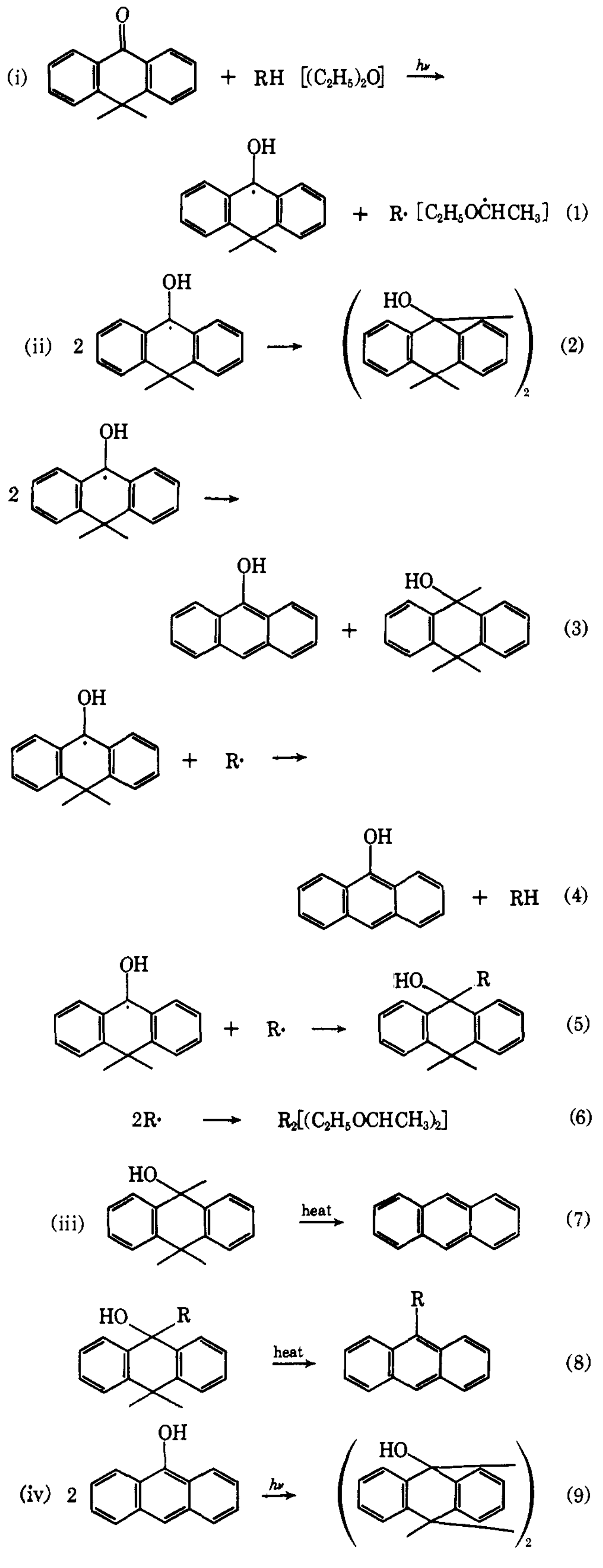
(12) About 80% of anthrone in ethereal solution was found to be converted into the ketyl radical by a flash irradiation.

(13) The yield (%) was determined as the ratio of each product to the whole product. The latter is taken to be equal to the decreased amount of anthrone caused by light irradiation.

(14) Besides the two main products, a small amount of unknown product (below 10% of the products) was found.

(15) R. M. Hochstrasser and G. B. Porter, *Quart. Rev.* (London), **14**, 146 (1960).



yield was determined to be 20%. The uv spectrum of the sample shown in Figure 5 has a band at ~260 mμ which corresponds to the $^1B_{2u} \leftarrow {}^1A_{1g}$ band of benzene. This is reasonable in view of the structure of anthrapinacol. The ir spectrum of the sample (curve b in Figure 6) confirms the existence of the –OH and $>CH_2$ groups. The nmr spectrum of the sample in DMSO shows the existence of the phenyl (τ ~3.0), –OH (τ 4.1), and $>CH_2$ (τ 6.9) groups. The remaining 10% of products might correspond to unknown substances which appeared after the above-mentioned two eluates in gas chromatography.

From both experiments, we can safely conclude that anthranol and anthrapinacol are the main products of photochemical reaction in the ethereal solution of anthrone, though a small amount (<10%) of unknown product is obtained.

Reaction Mechanism. From the reactive intermediate, its decay curve, and the reaction products, the possible reaction paths for the photoinduced isomerization of anthrone can be schematically shown as follows.

Reaction 1 which is the abstraction of hydrogen from ethyl ether by the triplet anthrone is substantiated by the detection of the anthrone ketyl radical as the reaction intermediate. Reaction 2 is necessary for the formation of anthrapinacol detected as one of the main products. Anthranol can be produced by reaction 3 and/or reaction 4. Reaction 9 is the photodimerization process of anthranol to dianthranol. This process can safely be disregarded for the experiment by a flash.

The identification of the unknown products was next considered. It is well known that 9,10-dihydroanthranol and its derivatives change easily into anthracene and its derivatives with the elimination of water.[16] Therefore the substances which might be formed through reactions 3 and 5 should change into anthracene and its derivatives through reactions 7 and 8 on "flashed and boiled solution." In actuality, however, the "flashed and boiled" solution does not exhibit the absorption spectrum corresponding to the 380-mμ band of anthracene. This means that reactions 3, 5, 7, and 8 can be actually disregarded. As a whole, we present the reaction mechanism consisting of reactions 1, 2, 4, and 6 for the isomerization of anthrone by a flash.

Determination of Rate Constants. In order to understand the reaction process more accurately and to determine the rate constants, the kinetic analysis was carried out with the aid of the above-mentioned reaction mechanism, in particular by reactions 2, 4, and 6.

$$-\frac{dx}{dt} = k_2x^2 + k_4xy$$

$$-\frac{dy}{dt} = k_4xy + k_6y^2$$

Here, x and y are concentrations of the ketyl radical and the R radical, respectively, and k_2, k_4, and k_6 are rate constants for reactions 2, 4, and 6, respectively.

These equations cannot strictly be solved, but the following approximate solutions can be obtained on the assumption of $k_2, k_4 \gg k_6$ which is reasonable from the experimental facts that both anthranol and anthrapinacol are the main reaction products and that the decay of the anthrone ketyl radical deviates from the second-order reaction formula with the progress of reaction. For the initial stage immediately after flashing, we can put $x = y$ and obtain the second-order reaction formula shown in eq 10.

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(16) F. Krollpfeiffer and F. Bransheid, *Ber.*, **56**, 1617 (1923).

$$x = \left[(k_2 + k_4)t + \frac{1}{x_0}\right]^{-1} \qquad (10)$$

Here x_0 is the initial concentration of the ketyl radical and is taken to be equal to the decrease in the amount of anthrone caused by a flash irradiation.

With the progress in the reaction, x decreases more rapidly than y, and therefore in some stage of the reaction the latter may approximately be regarded as a constant in spite of the change in x. For this stage, we can obtain the following equation for the first-order reaction.

$$x = x_0 e^{-k_4 y t} \qquad (11)$$

The above result is consistent with the experimental fact that the reaction proceeds following the second-order formula at the initial stage and the first-order one at the next stage. The average second-order rate constant $K = k_2 + k_4$ in eq 10 was found to be 11 (± 2) $\times$ 10^7 M^{-1} sec^{-1} from the gradient at $t \simeq 0$ of the $1/A - t$ curve. As the reaction proceeds, the decay curve gradually deviates from the linear relationship between $1/A$ and t expected from eq 10. This is because x decreases more rapidly than y, and the approximate condition of $x \approx y$ necessary for the derivation of eq 10 does not hold at some stage in the reaction. When the reaction proceeds further, it follows eq 11 and the first-order rate constant $K' = k_4 y$ can be obtained from the log $A - t$ curve shown in Figure 4. The K' value is expected to greatly depend on y and therefore on the initial concentration of anthrone. In actuality we found that it monotonously increases from $\sim$1 sec^{-1} to $\sim$10 sec^{-1} with the increasing concentrations of the solutions of 10^{-5} to 10^{-4} M.

From the data of the yields (40% for anthranol and 60% for anthrapinacol) of products by a flash irradiation and the second-order rate constant (K), we could determine the values of k_2 and k_4 separately as follows (at 25°).

$$k_2 = 7\,(\pm 1) \times 10^7\ M^{-1}\ \text{sec}^{-1}$$

$$k_4 = 4\,(\pm 1) \times 10^7\ M^{-1}\ \text{sec}^{-1}$$

The value of k_2 is consistent with the value observed by Beckett and Porter[17] for benzophenone in isopropyl alcohol. They determined the rate constant for the pinacolization of the benzophenone ketyl radical to be 5.9 $\times$ 10^7 M^{-1} sec^{-1}.

Acknowledgment. We gratefully acknowledge Dr. A. Tahara and Dr. N. Ikegawa of the Institute of Physical and Chemical Research for their kind discussions and kind help in the gas chromatography experiment.

(17) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963).

Kinetics of Proton-Transfer Reactions of Amino Acids and Simple Polypeptides[1]

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Abstract: The velocity and attenuation of 3-100-MHz ultrasonic waves propagating in aqueous solutions of glycine, diglycine, triglycine, β-alanine, and γ-aminobutyric, aspartic, and glutamic acids have been measured as a function of pH. No dispersion is observed but excess acoustic absorption characterized by a relaxation time between 2.8 $\times$ 10^{-9} sec (for γ-aminobutyric acid) and 3.2 $\times$ 10^{-8} sec (for triglycine) is found. From the dependence of the absorption on pH it is deduced that perturbation of the proton-transfer equilibrium, $R\text{-}NH_3^+ + OH^- \rightleftharpoons R\text{-}NH_2 + H_2O$, is the process responsible, and values of k_f, k_b, and the standard volume change are determined.

The proton-transfer reactions of the amino acids and simple polypeptides

$$\underset{\text{ZH}}{^-OOC\text{-}R\text{-}NH_3^+} + OH^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \underset{\text{Z}^-}{^-OOC\text{-}R\text{-}NH_2} + H_2O \qquad (1)$$

constitute a simple related series of reactions amenable to study by ultrasonic absorption techniques offering an interesting variety of possibilities for the observation of the effects of the charge, polarity, and flexibility of R on the rate constants. We have measured the acoustic absorption in solutions of glycine, diglycine, triglycine, β-alanine, and γ-aminobutyric, L-aspartic, and L-glutamic acids. The dependence of the absorption on pH is found to imply that perturbation of the proton-transfer equilibrium is the process principally responsible for the attenuation of sound. We will attempt to rationalize the rate constants deduced from the observedre laxation times in terms of the mechanism

$$^-OOC\text{-}R\text{-}NH_3^+ + OH^- \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} {}^-OOC\text{-}R\text{-}NH_3\text{-}OH \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} {}^-OOC\text{-}R\text{-}NH_2 + H_2O \qquad (2)$$

the rate of the first step of which involves the diffusional encounter of the amine and OH^- to form a H-bonded ion pair being relatively insensitive to the nature of R.

Ultrasonic Attenuation

In the absence of significant dispersion the frequency dependence of the ultrasonic attenuation (α) due to a

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(1) K. F. Herzfeld and T. A. Litovitz, "Absorption and Dispersion of Ultrasonic Waves," Academic Press, New York, N. Y., 1959.