Effects of Basic Substances on the Rate and Equilibrium of the Tautomeric Reaction between Anthrone and Anthranol

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(Received June 8, 1964)

The rate and equilibrium of the keto-enol tautomeric reaction in solution between anthrone and anthranol are known to be strongly dependent upon the solvent employed.[1] In hydrocarbons the reaction is so slow that it requires several days to reach the equilibrium, starting from one of the tautomeric pair. This makes it practically impossible to determine the equilibrium constant, *K*, in such inert solvents. We have recently observed spectroscopically, however, that the tautomeric reaction in hydrocarbon solvents is markedly affected both in rate and in equilibrium by the presence of basic substances.

The absorption spectrum of anthrone in benzene is shown in Fig. 1, together with the spectrum of the equilibrium mixture of anthrone and anthranol. The equilibrium was established by the addition of a small amount of triethylamine to the benzene solution, the concentration of the amine being only 10^{-4} mol./l. Triethylamine of this low concentration sufficiently accelerates the keto-enol transformation, the rate being increased by a factor of 10^3, but it exerts almost no influence on the equilibrium itself. Consequently, from an analysis of the absorption spectra, the equilibrium constant could be determined to be $K=0.0025$ at 20°C in benzene. In the same way we obtained $K=0.0021$ at 20°C in isooctane. Furthermore, the temperature dependence of the *K* values led to the following ΔH values: $\Delta H=2.6$ kcal./mol. in benzene and $\Delta H=3.3$ kcal./mol. in isooctane. Both the *K* and ΔH values indicate that the keto form is more stable than the enol form in hydrocarbons. The present experimental data will be useful in dealing with the problem of keto-enol tautomerism in general.[2,3]

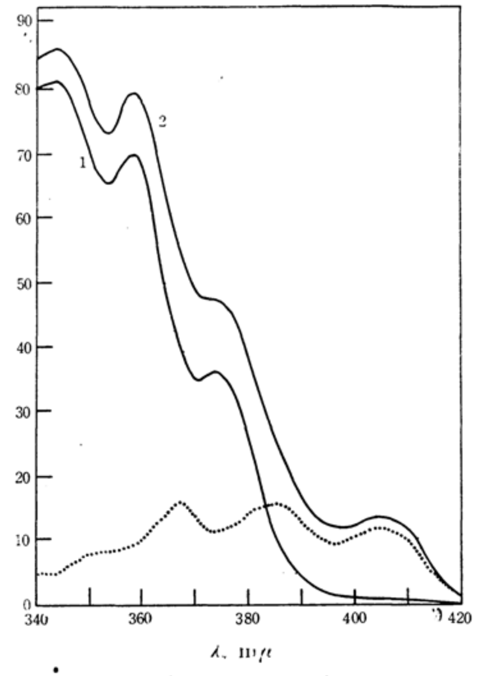

Fig. 1. Absorption spectra of anthrone and the equilibrium mixture of anthrone and anthranol in benzene at 20°C. Solid curve 1, anthrone; solid curve 2, the equilibrium mixture; dotted curve, difference of absorptions 2 and 1, corresponding to the absorption due to anthranol.

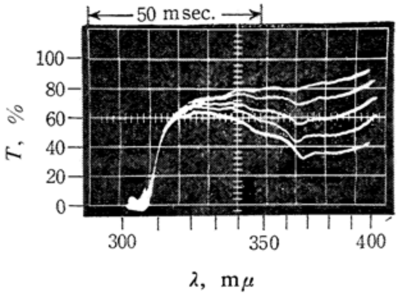

Fig. 2. Spectrophotometric tracing of the base-catalyzed transformation reaction from anthrone to anthranol. The spectra from top to bottom are at 1.5, 4.5, 10, 20, and 120 sec., respectively, after mixing of isooctane solution of anthrone and the same solution of triethylamine. The concentrations of anthrone and triethylamine at the beginning of the reaction are, respectively, 6.1×10^{-4} and 0.9 mol./l. The cell length is 11 mm. and the temperature is 24°C.

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[1] Y. Bansho and K. Nukada, This Bulletin, 33, 579 (1960); K. Nukada and Y. Bansho, ibid., 26, 454 (1953).

[2] B. Pullman and A. Pullman, "Quantum Biochemistry," Interscience, New York (1963), pp. 121-123.

[3] A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, New York (1961), pp. 248-255.

The equilibrium between anthrone and anthranol is affected by the amine with higher concentrations. It is noticeably displaced to the side of the enol form with an increasing concentration of added amine. Thus, for the amine concentration of 1 mol./l., the enol form amounts to about 10 per cent of the keto form. This phenomenon can be satisfactorily interpreted as due to the formation of a hydrogen bond between the enol form and the amine. When the concentration of triethylamine is of the order of 10^{-1} to 1 mol./l., the tautomeric equilibrium is reached in isooctane within one or two minutes. The keto-enol reaction was traced by the use of a rapid-scan spectrophotometer[4] constructed recently in our laboratory; this spectrophotometer can display transmission curves on a cathode-ray tube for the wavelength region from 220 to 650 mμ, with a scanning time of 0.3 sec. The results are given in Fig. 2, from which it can be seen that the reaction is of the first order.

Several other basic compounds have also been investigated. Pyridine has essentially the same effect as in the case of triethylamine on both the reaction rate and the equilibrium. Dioxane produces no appreciable change in the reaction rate, but it has a definite effect on the keto-enol equilibrium. Details of the work will be published later.

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[4] H. Baba and Y. Shindo, *Bull. Res. Inst. Appl. Elec., Hokkaido Univ.*, **15**, 107 (1963).