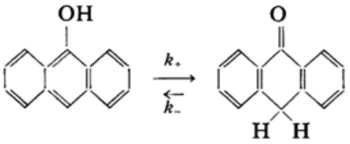
Kinetic Study on Isomerization of Anthranol to Anthrone

By Yoshié BANSHO and Kenkichi NUKADA

(Received October 13, 1959)

Only a few studies concerning the physical and chemical properties of anthranol have been reported in literature. K. H. Meyer[1] found in 1911 that in organic solvents anthranol turns to anthrone and after a long time a chemical equilibrium between these substances is established. Bäckström et al.[2] pointed out an iodine titration method for the analysis of anthranol. Le Fèvre et al.[3] investigated the dielectrical properties of the same substance, but its purity was not satisfactory enough to determine the dielectric constant of the solutions.



Anthranol Anthrone

The authors have established the best condition for the preparation of anthranol and measured the dipole moments in several organic solvents[4].

In this paper, the authors present the methods of measuring the velocity constants of the isomerization of anthranol to anthrone by the analytical and dielectrical techniques and the calculated values of the activation energies of the reaction.

Experimental

Preparation of Anthranol. — Improving the original procedures of Meyer[1] and Bäckström et al.[2], the authors have established the best method of preparation of pure anthranol and reported the findings in this Bulletin[4].

Measurements of Velocity Constants of the Isomerization by Iodometry.—Bäckström et al. determined the purity of anthranol by iodometric analysis. This suggests that the method may also be used for the measurement of isomerization velocity, because one mole of anthranol reacts exactly with one mole of iodine in some solvents, while anthrone does not react with iodine at all. It has been found that methanol and ethanol were suitable solvents for the measurement of isomerization velocity.

In a stream of nitrogen, 1.0 g. of freshly prepared anthranol was dissolved into 200 cc. of solvent keeping the temperature constant. After appropriate time, 10 cc. of the solution was poured into 5 cc. of 0.1 N iodine-potassium iodide aqueous solution. After a few minutes the remaining iodine was titrated with 0.1 N sodium thiosulfate solution, and thus the content of anthranol in the solution was obtained directly. These operations were repeated until an equilibrium of the reaction was attained.

Dielectrical Measurement.—The authors have already measured the apparent dipole moments of anthranol in several organic solvents at 6 and 15°C[4]. At these temperatures, isomerization velocities are so small that anthranol in solvents safely remains unchanged during the measurements.

When the temperature is raised, the reaction velocity of isomerization becomes greater and it becomes impossible to get the real value of dipole moment of anthranol. A kinetic study of isomerization, on the other hand, becomes possible even at elevated temperatures.

Dielectric constants of solutions (in benzene and toluene) at several temperatures were measured several times until they reached maximum values. Although it is necessary also to measure the densities of solutions at every time of measurements of dielectric constants, this procedure is very troublesome. Hence, in this paper, it was assumed that the density of solutions remained constant during the reaction.

Results and Discussion

Iodometry.—First of all, it was assumed that the reaction is reversible and of the first order, so that

$$\frac{\mathrm{d}x}{\mathrm{d}t}=k_+(a_0-x)-k_-(a_0'+x) \qquad (1)$$

where x is the amount of changed anthranol at the time t, a_0 and a_0' are the initial amounts of anthranol and anthrone expressed in molar fraction, and k_+ and k_- are the velocity constants of normal and reverse reactions, respectively. As the purity of the anthranol was about 98%,

$$a_0 \fallingdotseq 1 \quad \text{and} \quad a_0' \fallingdotseq 0$$

and then

$$K=\frac{k_+}{k_-}\fallingdotseq\frac{a_\infty}{1-a_\infty} \qquad (2)$$

where K is the equilibrium constant and a_∞ is the value of x at the equilibrium ($\mathrm{d}x/\mathrm{d}t=0$).

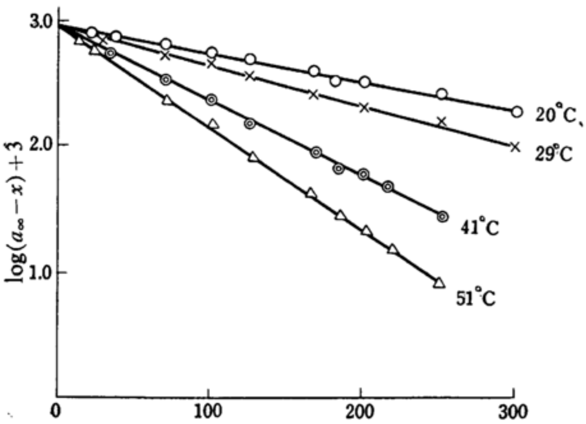
---

[1] K. H. Meyer, *Ann.*, **379**, 37 (1911).

[2] H. Bäckström and H. Beatty, *J. Phys. Chem.*, **35**, 2549 (1930).

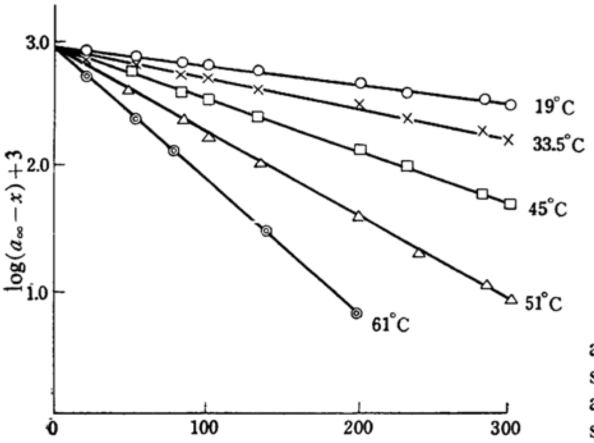
[3] C. L. Angyl and R. J. W. Le Fèvre, *J. Chem. Soc.*, **1950**, 562.

[4] K. Nukada and Y. Bansho, This Bulletin, **26**, 454 (1953).



Time (min.)

Fig. 1. Kinetics in methanol by iodometry.



Time (min.)

Fig. 2. Kinetics in ethanol by iodometry.

TABLE I. THE VELOCITY CONSTANTS OF ISOMERIZATION

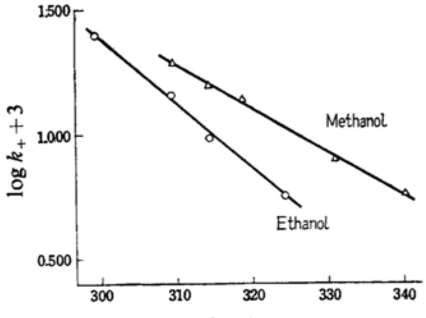
Temp., °C	In methanol k_+	In ethanol k_+
20	0.0050	0.0032
29	0.0063	
36		0.0050
41	0.0125	0.0059
45	0.0137	0.0079
51	0.0165	0.0149
61	0.0256	0.0211

From Eqs. 1 and 2, the next equation is obtained.

$$k_+ + k_- = 1/t \ln [a_\infty/(a_\infty - x)] \qquad (3)$$

From Eqs. 2 and 3, the value of k_+ can be obtained. In Figs. 1 and 2, $\log(a_\infty - x)$ are plotted against t at between 20~60°C in methanol and ethanol solutions, respectively. Since rectilinear relationships between $\log(a_\infty - x)$ and t were observed, it is reasonable to assume that the reaction of isomerization is of the first order. The calculated values of k_+ are shown in Table I.

According to Arrhenius' equation, the authors plotted the values of $\log k_+$ against the reciprocal of absolute temperature $(1/T)$ as shown in Fig. 3 and calculated the activation energies of the isomerizations of anthranol in methanol and ethanol. Anthranol isomerizes faster in methanol than in ethanol and the obtained values of activation energies are 5.8 and 12.4 kcal./mol. in methanol and ethanol, respectively. This might be due to the fact that ethanol is stronger in basisity than methanol.



$1/T \times 10^5$

Fig. 3. Measurements of activation energies by iodometry.

The times required for the complete disappearance of fluorescence in diluted anthranol solutions were ca. 50 and 6.5 hr. in ethanol and methanol, respectively[4]. These times are supposed to depend upon the velocities of isomerization.

Dielectrical Measurement.—The only measurable quantity with dielectrical measurement is the time dependency of the dielectric constant of solutions at various temperatures. In order to obtain the velocity constants from these measurable quantities, some assumptions are made.

First of all, it was assumed that

$$p_{12}(t) = (1-y)p_1 + yp_2(t) \qquad (4)$$

where $p_{12}(t)$, p_1 and $p_2(t)$ are the specific molecular polarizations of solution, solvent and solute, respectively, and y is the weight fraction, of solute. The molecular polarization of solute $P_2(t)$ is obtained by substituting the following Eqs. 5—7 into Eq. 4.

$$p_{12}(t) = 1/d_{12} \times (\varepsilon_{12}(t) - 1)/(\varepsilon_{12}(t) + 2) \qquad (5)$$

$$p_1 = 1/d_1 \times (\varepsilon_1 - 1)/(\varepsilon_1 + 2) \qquad (6)$$

$$p_2 = P_2(t)/M \qquad (7)$$

where $\varepsilon_{12}(t)$, ε_1 and d_{12}, d_1 are dielectric constants and densities of solution and solvent, respectively, and M is a molecular weight of

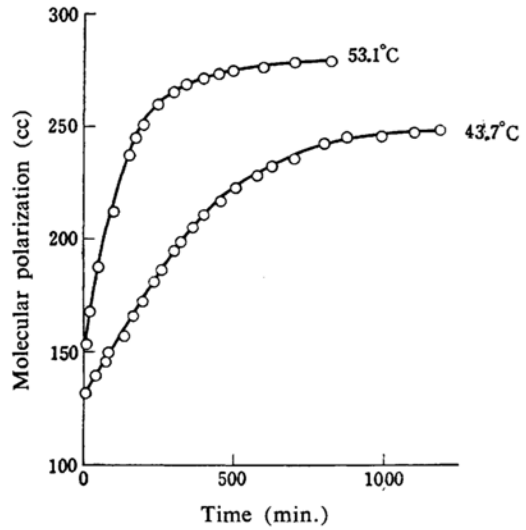


Fig. 4. The change of molecular polarization in benzene.

solute. $p_{12}(t)$, $p_2(t)$, $P_2(t)$ and $\varepsilon_{12}(t)$ mean that these quantities are functions of time. In Fig. 4, $P_2(t)\sim t$ curves are shown.

If the reaction is of the first order, Eq. 3 leads

$$\exp(-kt_i)=1-x(t_i)/a_\infty \tag{8}$$

where $k=k_+ + k_-$ and $i=1,2,3,\ldots\ldots,N$ (N is the number of measurement). If it is possible to measure $x(t)$, the two unknown parameters k and a_∞ in Eq. 8 can be determind by the statistical method of least square, and then with Eq. 2 the normal velocity constant k_+ can be calculated. In the dielectrical measurement, however, $x(t_i)$ can not be obtained directly but only $P_2(t)$ can be measured. So it is necessary to combine the above quantities using a further assumption as follows:

$$P_2(t)=P_L[1-x(t)]+P_N x(t) \tag{9}$$

where P_L and P_N are the molecular polarizations of pure anthranol and pure anthrone, respectively, and both are unknown parameters. From Eq. 9, it is obtained the following equations.

$$x(t)=(P_2(t)-P_L)/(P_N-P_L) \tag{10}$$

With $t=\infty$ the authors have $x=a_\infty$, so that

$$a_\infty=(P_2(\infty)-P_L)/(P_N-P_L) \tag{11}$$

where $P_2(\infty)$ means the saturated $P_2(t)$ value. Substituting Eqs. 10 and 11 to Eq. 8, it is obtained

$$\exp(-kt_i)=(P_2(\infty)-P_2(t_i))/(P_2(\infty)-P_L) \tag{12}$$

Eq. 12 includes two unknown parameters (k and P_L) but they can be obtained by the statistical method of least square. In the present case the velocity constant of the reverse reaction is found to be very small compared with that of the normal reaction*. Therefor, k_+ is almost equal to k and the final equation is obtained.

$$k_+ \doteqdot k = \frac{\sum_i \ln(P_2(\infty)-P_2(t_i)) \sum_i t_i/N - \sum_i t_i \ln(P_2(\infty)-P_2(t_i))}{\sum_i t_i^2 - (\sum_j t_i)^2/N} \tag{13}$$

If Arrhenius' equation is also valid in this cace, the curve $\ln k_+ \sim 1/T$ should be linear and the results agree quite well with this requirement (Fig. 5). Activation energies, obtained from Fig. 5 are listed in Table II. These values are of the same order as those obtained in methanol and ethanol solutions by the iodine titration method. It is important to notice that the potential barrier between two isomers is rather small so that the isomerization can occur very easily.

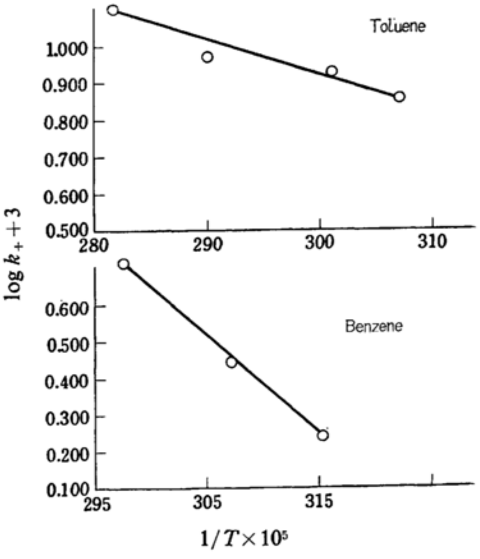


Fig. 5. Measurements of activation energies by dielectrical method.

TABLE II. THE ACTIVATION ENERGIES OF ISOMERIZATION MEASURED IN SEVERAL ORGANIC SOLVENTS

Solvent	Method of measurement	Activation energies kcal./mol.
Methanol	Iodometry	5.8
Ethanol	Iodometry	12.4
Benzene	Dielectrical method	12.2
Toluene	Dielectrical method	4.8

The authors could not find common solvents suitable to measure the velocity constant for

---

* The authors measured the molecular polarization of anthrone in benzene and toluene and ascertained that $P_2(t)$, in this case, maintained its initial value even after a long time, i. e. k_- was almost equal to zero.

both the analytical and dielectrical methods for the following reasons: methanol and ethanol are polar substances and not suitable for the dielectrical measurement, while benzene and toluene are immiscible with water making iodometry titration impossible.

Conclusion

Pure anthranol was prepared and its isomerization to anthrone was studied by analytical and dielectrical methods. The reaction was found to be of the first order and the observed heat of activations were 5.8, 12.4, 12.2 and 4.8 kcal./mol. in methanol, ethanol, benzene and toluene, respectively. These small values mean that anthranol isomerizes easily in these solvents.

Sincere thanks are tendered to Dr. Y. Mashiko of this Institute for his valuable discussion. The authors also appreciate the help rendered by Mr. Kuang Lieh Huang in performing a part of these experiments.

Government Chemical Industrial
Research Institute of Tokyo
Hatagaya, Shibuya-ku, Tokyo