Synthesis and Dielectric Polarization of 9-Anthranol

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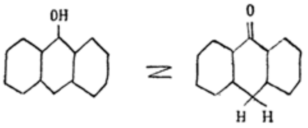
(Received June 23, 1953)

Introduction

K. H. Meyer reported in 1911 on the synthesis of 9-anthranol, which is the simplest substance in leuco-compounds of anthraquinone series, and also on its behaviour in several organic solvents.[1] He observed that 9-anthranol exhibited strong fluorescence in some solvents and explained that there might exist in solution a chemical equilibrium between anthrone and 9-anthranol, the reaction velocity and equilibrium constant of which depended on solvent. Bäckström et al. pointed out an iodine titration method for the quantitative analysis of 9-anthranol.[2] Le Fèvre et al. investigated the dielectric behaviour of the same substance and its methyl ether. However, the above-mentioned authors could not prepare pure 9-anthranol. The present authors have established the best condition of synthesis of 9-anthranol and measured the dipole moment of it by the solution method. The reproducibility was satisfactory.



9-Anthranol Anthrone

Fig. 1

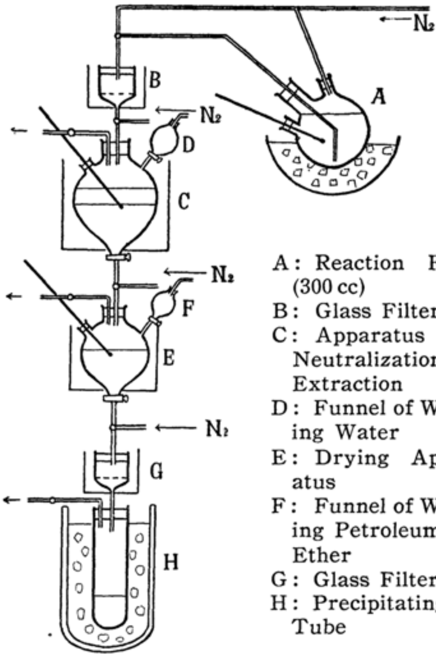
Experimental

Synthesis

The original procedure of Meyer[1] and the modified one of Bäckström and Beatty[2] have been traced, but the purity of 9-anthranol prepared in this way was unsatisfactory. The authors have synthesized 9-anthranol of high purity by improving these two methods. They have found that it was important to operate the synthesis continually in a stream of nitrogen (to prevent oxidation) and to maintain the temperature as low as possible (to prevent isomerisation) during the preparation. The result of synthesis had good reproducibility.

Anthrone was prepared from anthraquinone (Org. Syn. Coll. vol. 1, p. 60) and recrystallised twice from mixed solvent of benzene and petroleum ether (3:1). m.p. 154.7°C.

The apparatus is shown schematically in Fig. 2, and the procedure is as follows:



A: Reaction Flask (300 cc)
B: Glass Filter
C: Apparatus for Neutralization and Extraction
D: Funnel of Washing Water
E: Drying Apparatus
F: Funnel of Washing Petroleum Ether
G: Glass Filter
H: Precipitating Tube

Fig. 2. Apparatus for Synthesis of 9-Anthranol

3.0 g. of fine powdered anthrone was boiled in 180 g. of 10% aqueous solution of sodium hydroxide for about ten minutes in a stream of nitrogen, and as soon as the boiling was over, 300 g. of ice pieces were added and the flask was cooled rapidly by an ice sodium chloride bath set outside. When the temperature of the solution lowered to −5°C, the flask was arranged as indicated in Fig. 2, A, and cooled to maintain this temperature.

Apparatus for neutralization and extraction, C, which contained 120 cc. of toluene, 300 cc. of distilled water, 300 g. of ice pieces and 15 cc. of 98% sulphuric acid, was cooled from outside by solid carbon dioxide to maintain −5°C. The solution of sodium salt of 9-anthranol was poured directly into C in a stream of nitrogen and shaken; the

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

2) H. Bäckström and H. Beatty, *J. Phys. Chem.*, **35**, 2549 (1949).

3) C. L. Angyal and R. J. W. Le Fèvre, *J. Chem. Soc.*, **1950**, 562.

precipitated 9-anthranol was extracted in upper toluene layer. Then by the pressure of nitrogen the water layer was removed, the toluene iayer was washed with 200 cc. of distilled water and the water layer was removed similarly. The yellow emulsion was sent into a drying apparatus F which contained 80 g. of fresh calcined and oxygen-free anhydrous sodium sulphate, and was shaken at −5°C. 20 cc. of petroleum ether (b.p. 60∼70°C.) was cooled beforehand at ca. −70°C. in a precipitating tube H which was immersed in a solid carbon dioxide-methanol bath; the clear dried 9-anthranol toluene solution was then poured into petroleum ether through the glass filter G by the suction and the pressure of nitrogen. Sodium sulphate was washed with 60 cc. of petroleum ether (b.p. 60∼70°C) and solution in H was diluted simultaneously. The pale yellow precipitate of 9-anthranol was deposited immediately and the precipitation was accomplished in an hour. The precipitate was filtered in a stream of nitrogen as rapidly as possible, washed with 50 cc. of petroleum ether (b.p. 45∼50°C), then taken in a vacuum desiccator and sucked by a vacuum pump for half an hour at 0°C to remove petroleum ether contained in crystal. Then the product was dried for about ten hours over phosphorous pentoxide in a vaccum at the same temperature. The yellow fine crystal of 9-anthranol was enclosed in ampouls in a stream of nitrogen. yield: 1.5—1.7 g.

Infrared spectrum of 9-anthranol suspended in Nujol was measured and a strong absorption band of OH group was observed.

Notice

1) Water and toluene used in the synthesis were distilled in a stream of nitrogen, so that they were free from oxygen.

2) It was necessary to cool all the apparatus, A to G, at −3 ∼ −5°C by small pieces of solid carbon dioxide.

3) All the transfusions of liquid were made in a closed apparatus by the suction or under the pressure of nitrogen, and the whole time of preparation was within half an hour.

4) Oange-yellow to red crystal was deposited, if the temperature rose or the air leaked into the apparatus. The product prepared in this way could not be used as a sample for the measurement of dielectric constant because the reproducibility of results was unsatisfactory.

Behaviour in Solvent

9-Anthranol was dissolved in several solvents and the times *t*'s required for the complete disappearance of fluorescence of solutions were measured. (Table 1). According to Meyer,1) *t* was a function of the reaction velocity of tautomerism.

In ethanol, dioxane and ether *t*'s were large and the reactions were supposed to be slow. However in carbon disulphide, carbon tetrachloride, acetone and pyridine no fluorescence appeared and the reactions were supposed to be very fast. In benzene *t* was large and as the number of methyl groups of benzene ring increased, *t* decreased. In petroleum ether, n-heptane and cyclohexane *t*'s were large but practically these solvents could not be used in the dielectric measurement because the solubilities in these were very small.

As the suitable solvents the authors then chose benzene, dioxane and toluene for the following experiments.

Table 1

The Times Required for the Complete Disappearance of Fluorescence at 7°C.

Solvent	Solubility	*t* (hours)
Benzene	+	22
Toluene	+	10
m-Xylene	+	5
Chlorobenzene	+	0.5
Methanol	+	6.5
Ethanol	+	ca. 50
n-Buthanol	+	7
i-Amyl Alcohol	+	17
Ether	+	24
Dioxane	++	ca. 60
Petroleum Ether (b.p. 40∼60°C.)	−	24
n-Heptane	−	24
Cyclohexane	−	23
Acetic Acid	+	1
Chloroform	+	0.2
Carbontetrachloride	+	No fluorescence
Carbon Disulphide	+	"
Acetone	+	"
Pyridine	++	"

The symbols are: ++ very great, + ordinary, − very small.

Dielectric Measurements

Solvent: All the solvents were purified according to the methods in "Organic Solvents".4)

Density: Ostwald-type pycnometer was used.

Instrument: Usual Heterodyne-beat type oscillator designed and constructed by one of the authors (Nukada) was used to measure dielectric constants of solutions.5) Capacities of sample cells were from 50 pF to 80 pF.

The synthesized sample had to be stored in nitrogen atomosphere at low temperature and to be dissolved in solvents as quickly as possible. When the purity of a sample was low or the temperature of solution too high, 9-anthranol changed into anthrone and the fluorescence of the solution vanished rapidly.

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4) A. Weissberger and E. Proskauer, "Organic Solvents", Oxford University Press, 1935, p. 106, 107, 140.

5) e.g. see J. W. Baker and L. Groves, *J. Chem. Soc.*, **1939**, 1144.

Table 2

The Dielectric Constants and the Densities of 9-Anthranol in Several Organic Solvents.*) **) ***)

i) Solvent: Benzene, 6.3°C.

ω	ε_{12}	v_{12}
0.01297	2.345	—
0.00885	—	1.1164
0.00485	2.325	1.1178
0.00165	2.318	1.1190

$\varepsilon_1=2.313$ $v_1=1.1193$
$\alpha=23.0$ $\beta=-0.397$
$p_{20}=0.634$ $P_{20}=123$ cc
$\mu=1.72$ D

ii) Solvent: Benzene, 15°C.

ω	ε_{12}	v_{12}
0.02197	—	1.1240
0.01654	2.338	—
0.01299	2.330	—
0.00877	2.317	1.1281
0.00860	2.315	—
0.00520	2.309	1.1295
0.00386	2.304	—
0.00234	—	1.1303
0.00165	2.299	—

$\varepsilon=2.294$ $v_1=1.1309$
$\alpha=26.7$ $\beta=-0.332$
$p_{20}=0.73$ $P_{20}=142$ cc
$\mu=1.99$ D

iii) Solvent: Dioxane, 15°C.

ω	ε_{12}	v_{12}
0.01424	2.336	0.9578
0.01044	—	0.9588
0.00380	2.306	0.9605
0.00229	2.303	0.9610

$\varepsilon_1=2.298$ $v_{12}=0.9614$
$\alpha=26.7$ $\beta=-0.264$
$p_{20}=0.63$ $P_{20}=122$ cc
$\mu=1.82$ D

iv) Solvent: Benzene-Dioxane Mixture, 15°C
(Mol fraction B : D = 10 : 1)

ω	ε_{12}	d_{12} (g/cc)	P_2 (cc)
0.01555	2.352	0.9089_2	162
0.01296	2.341	0.9076_8	159
0	2.295	0.9028_5	—

$P_{20}=161$ cc $\mu=2.20$ D

v) Solvent: Benzene-Dioxane Mixture, 15°C
(Mol fraction B : D = 100 : 1)

ω	ε_{12}	d_{12} (g/cc)	P_2 (cc)
0.02150	2.350	0.8979_9	138
0.00914	2.313	0.8935_7	132
0	2.291	0.8911_8	—

$P_{20}=135$ cc $\mu=1.91$ D

vi) Solvent: Toluene, 15°C.

ω	ε_{12}	d_{12} (g/cc)	P_2 (cc)
0.02117	2.444	0.8788	115
0.01605	2.440	0.8776	128
0.00826	2.426	0.8767	134
0.00409	2.409	0.8728	132
0	2.398	0.8713	—

$P_{20}=133$ cc $\mu=1.88$ D

*) The symbols used in this Table are the same as those of Halverstadt and Kumeler.⁷⁾ ε_{12}: dielectric constant of solution, $v_{12}\,(=1/d_{12})$: specific volume of solution (cc/gr), ω: concentration (weight percent), P_2: solute molar polarization, P_{20}: solute molar polarization at infinite dilution, p_{20}: solute specific polarization at infinite dilution: $\alpha=\frac{d\varepsilon_{12}}{d\omega}$, $\beta=\frac{dv_{12}}{d\omega}$, ε_1: dielectric constant of solution at infinite dilution, v_1: specific volume at infinite dilution, μ: dipole moment (Debye unit).

The values of α, ε_1, β and v_1 were calculated utilizing the statistical method of least squares.

**) In calculation of the orientation polarization the authors have assumed that the sum of electric polarization and atomic one was equal to the molar refraction MR_D for sodium D line. For 9-anthranol $MR_D=58$ cc.

***) μ were calculated as

$$\mu=0.0128\times\sqrt{(P_{20}-MR_D)T}$$

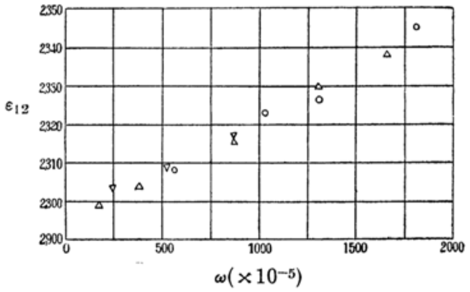

Fig. 3. Relation between ω and ε_{12}
Solvent: Benzene. 15°C.

Symbols △, ▽ and ○ represent the results of several experiments under the same condition.

Results

Dielectric constants and densities of several solutions were measured at various concentrations. (Table 2).

All the $\omega\sim\varepsilon_{12}$ curves became straight lines except for toluene solution.⁶⁾

The dipole moments of 9-anthranol in benzene and dioxane solutions were calculated by Halverstadt-Kumler's equation⁷⁾ and the moments in other solutions by the usual method.⁸⁾ The results are in Table 3. Since in solutions there exists a chemical equilibrium

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6) Fig. 3 shows the result of several measurements under the same experimental condition. Unlike the case of other samples, (e.g. anthrone in benzene, Denys, I. Coomber and J. R. Partington, *J. Chem. S.oc*, **1938**, 1444,) the curves were not fine straight lines. This deviation means probably the unstability of 9-anthranol in solvents.

7) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

8) P. Debye, "Polare Molekeln". Leibzig, 1929.

between 9-anthranol and anthrone, values in Table 3 do not mean the "exactly true value of dipole moment of 9-anthranol" but should be regarded as a "nearly true one", because in such solvents the velocity constants are small. Le Fèver et al. measured the dipole moment of 9-anthranol methyl ether. (1.5 D). Noting a difference of 0.4∼0.5 D between phenol and its methyl ether, they supposed that 9-anthranol had a moment of 1.9∼2.0 D.[3] The authors' result agrees with this supposition.

Table 3
The Dipole Moments of 9-Anthranol in Several Organic Solvents

Solvent	Temp	Moment (Debye Unit)
Benzene	6.3°C	1.72 D
Benzene	15 °C	1.99 D
Benzene : Dioxane (100 : 1)	15 °C	1.91 D
Benzene : Dioxane (10 : 1)	15 °C	2.20 D
Dioxane	15 °C	1.82 D
Toluene	15 °C	1.88 D

In benzene-dioxane mixture, the moment values are comparable with Nagakura and Baba's result on phenol.[9]

In toluene $\omega \sim \varepsilon_{12}$ curve was not a straight line.

It may be reasonable to explain the stabilisation of 9-anthranol by the assumption that in benzene[10] and dioxane[11] OH-group of 9-anthranol makes weak combination with solvent and the potential barrier between anthrone and 9-anthranol becomes higher, hydrogen atom of 9-anthranol's OH is thus hindered from shifting to the position "10" of anthracene ring. The results in Table 1 also support this asumption except for acetone and pyridine, in which the stabilisation of 9-anthranol by the combination O···H—O and N···H—O can be expected, but the causes of these exceptions are not plain now.

Summary

1) The condition of synthesis to obtain pure 9-anthranol was established.

2) Times required for the complete disappearance of fluorescence of solution were measured and assumed to be measures of reaction velocities of tautomerism from 9-anthranol to anthrone. In ethanol, ether, dioxane and benzene the reaction velocities were small.

3) Dielectric constants of 9-anthranol in benzene, dioxane, benzene-dioxane mixtures and toluene solutions were measured. Reproducibility was satisfactory. In the said solvents 9-anthranol was relatively stable and $\omega \sim \varepsilon_{12}$ curves were straight lines except in toluene.

4) The stability of 9-anthranol in solvent was supposed to be increased, by an interaction between π-electrons of solvent and proton of solute O—H group in the case of benzene, or by O···H—O combination in the case of dioxane.

The authors' thanks are due to the kind guidance of Mr. Y. Mashiko and Mr. E. Koike, the Technical Officials of this Institute, and Assistant Prof. S. Nagakura, Tokyo University and to the advices in experiment of Mr. S. Saeki and Mr. K. Fujii, this Institute.

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[9] S. Nagakura and H. Baba, *J. Am. Chem. Soc.*, **74**, 5693 (1952).

[10] There is a coupling of π-electrons of benzene with proton of OH-group in solute molecule. (W. Lütte and R. Mecke, *Z. Elektrochem.* **53**, 241 (1949).)

[11] In dioxane a hydrogen bond between solvent and solute may exist.