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Energy Transfer between Benzene and Toluene in the Singlet States at 90°K

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The fluorescence spectrum of toluene in benzene has been photographed at 90°K and analyzed accurately. Systematic studies of concentrations made it possible to estimate the efficiency of energy transfer from the singlet state of the host molecule to that of the guest molecule. The fluorescence spectrum of pure benzene has also been studied at 4.2°K and 90°K for comparison, and the effect of toluene as an impurity in the benzene spectra has been discussed.

Leach, Lopez-Campillo and Lopez-Delgado[1] studied the effect of occluded gas and the thermal treatment of a sample on the probability of electronic-energy transfer between benzene and toluene at 80°K. We have also studied electronic-energy transfer in the lowest excited singlet states of benzene and toluene and estimated the rate of energy transfer in the system.

Experimental

The benzene was purified by the way described in a previous paper.[2] Commercial benzene often contains toluene as an impurity at a concentration of about 10^{-2}—10^{-3} mol/*l*. The purification was repeated until no toluene bands in the fluorescence spectrum could be detected within the experimental limits employed in this work.

The toluene was purified according to the method of Schwalbe.[3] A gaseous mixture of nitric and nitrous oxide was introduced into toluene, and then 2% of sulfuric acid was added 2 or 3 hr later. The toluene was stirred for 5 min and then left standing for 15 min. The lower layer was removed. This operation was repeated three times. When the acid part became faint yellow, the toluene was washed with a dilute caustic soda solution until no color change was detected in the solution. It was then dried over calcium oxide and distilled.

The optical setup was exactly the same as that described previously.[2] A super-high-pressure Hg lamp (ORA CHM-12) was used as a light source, and the Hg 2537 Å was projected on a sample through a filter system. The sample solutions employed were 10^{-5}, 10^{-4}, 5×10^{-4}, 10^{-3}, 5×10^{-4}, 10^{-2}, 10^{-1}, and 1 mol/*l* of toluene in benzene. For comparison a solution of 10^{-3} mol/*l* of toluene in cyclohexane was also studied. A sample solution was cooled rapidly by liquid air. While it was being frozen in a cell, the cell was pumped so that all occluded gas in the solution was removed.

The fluorescence spectrum of toluene in benzene was photographed with a Shimadzu quartz spectrograph, QM-60. The exposure time was fixed as 1 hr with a slit width of 50 μ, and Eastman-Kodak 103 a-O plates were used.

Results and Discussion

The fluorescence spectrum of the benzene crystal and the spectrum of toluene in benzene at various concentrations were studied. The microphotometer tracing curves are shown in Fig. 1. The spectral data of toluene in benzene and in cyclohexane are given in Tables 1 and 2 respectively. The spectrum of toluene increases in intensity with an increase in the concentration. It is, therefore, possible to make a quantitative analysis of toluene in benzene. Commercial benzene often contains toluene as an impurity the concentration of which can be estimated by, for example, comparing the height of a band 0—623 of toluene with that of a band, 0—992, of benzene of the tracing curves assumed as intensity (since the spectrum of toluene overlaps that of benzene so extensively that it is impossible to integrate a band intensity). By the way, the 0–0 band of the benzene crystal was not photographed under these experimental conditions, its spectral position was determined with plates subjected to prolonged exopsure.

At a concentration of 10^{-5} mol/*l*, no toluene fluorescence, but rather benzene fluorescence, was observed under the present experimental conditions and only toluene fluorescence was photographed at concentrations of more than 10^{-1} mol/*l* of toluene in benzene. The fluorescence of benzene disappeared at concentrations between 3×10^{-2} and 4×10^{-2} mol/*l* of toluene.

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[1] S. Leach, A. Lopez-Campillo, R. Lopez-Delgado and Maria-Clandina Tomas-Magos, *Compt. rend.*, **263**, 1230 (1966).

[2] Y. Murakami and Y. Kanda, to be published.

[3] C. Schwalbe, *Chem. Zentr.*, **1905**, 1, 360.

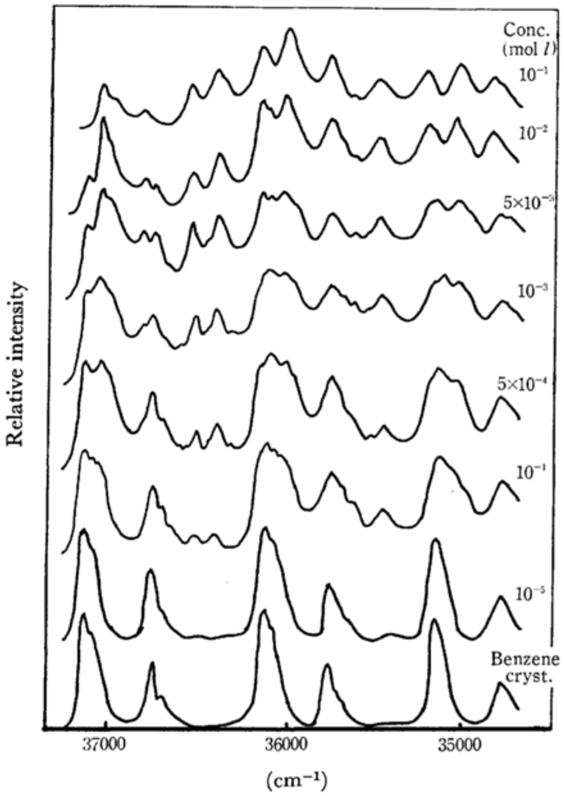

Fig. 1. Fluorescence spectra of toluene in benzene at various concentrations.

If there is no energy transfer from benzene to toluene, the ratio of the fluorescence intensity of toluene to that of benzene should be equal to the ratio of the molar fractions of toluene and benzene molecules, provided that the absorption coefficients of toluene and benzene at the wavelength of the excitation are the same and that the quantum

TABLE 1. FLUORESCENCE SPECTRA OF TOLUENE IN CYCLOHEXANE AT 77°K

Wave number No.	Wave number (cm^{-1})	$\Delta\nu$ (cm^{-1})	Assignment	Rel. Int.
1	37140	0	0–0.	5
2	36930	210	0–0.–220	2
3	36625	515	0–0.–520	6
4	36530	610	0–0.–623	8
5	36350	790	0–0.–788	10
6	36150	990	0–0.–1005	10
7	35930	1210	0–0.–1217	8
8	35775	1365	0–0.–1380	5
9	35735	1405	0–0.–623–788	5
10	35620	1520	0–0.–520–1005	6
11	35535	1605	0–0.–623–1005	7
12	35475	1665		6s*
13	35335	1805	0–0.–788–1005	8
14	35135	2005	0–0.–1005–1005	8
15	34940	2200	0–0.–1217–1005	6

* shoulder

TABLE 2. FLUORESCENCE SPECTRA OF TOLUENE AND BENZENE IN A MIXED SYSTEM AT 90°K

No.	Assignment (cm^{-1})			Relative intensity at various concentrations of tolunene (mol/l) 0,	10^{-5},	10^{-4},	5×10^{-4},	10^{-3},	5×10^{-3},	10^{-2},	10^{-1}
1	37826	0–0.*	(B)**	—	—	—	—	—	—	—	—
2	37220	0–0.–606	(B)	9	9	9	9	8	7	3	—
3	37100	0–0.	(T)	—	—	7s	9	9	10	7	4
4	36875	0–0.–220	(T)	—	—	—	—	5s	7	3	—
5	36835	0–0.–992	(B)	6	6	6	7	6	7	2	—
6	36575	0–0.–520	(T)	—	—	2	3	6	7	3	4
7	36475	0–0.–623	(T)	—	—	2	3	7	7	5	6
8	36305	0–0.–788	(T)	—	—	7s	8s	8s	10	9	8
9	36215	0–0.–606–992	(B)	10	10	10	10	10	9s	9s	—
10	36100	0–0.–1005	(T)	—	—	7s	9s	9	10	10	10
11	35885	0–0.–1217	(T)	—	—	—	—	8	8	8	8
12	35845	0–0.–2×992	(B)	5	4	8	8	—	—	—	—
13	35560	0–0.–520–1005	(T)	—	—	—	—	5s	6s	3s	4s
14	35480	0–0.–623–1005	(T)	—	—	5	3	7	7	6	5
15	35295	0–0.–788–1005	(T)	—	—	7s	8s	8s	9	7	6
16	35230	0–0.–606–2×992	(B)	9	9	8	9	9	—	—	—
17	35090	0–0.–2×1005	(T)	—	—	7s	8s	8s	9	7	6

s shoulder

* 37200 + 606 = 37826

** (B) and (T) are attributed to the bands of benzene and toluene, respectively.

yields of toluene and benzene are also the same. However, the numbers of benzene molecules are much greater than those of toluene molecules at the various concentrations employed here. This suggests that a considerable amount of energy transfer takes place from benzene to toluene.

The rate of energy transfer between toluene and benzene can now be calculated. Let us assume the following processes:

$$\begin{array}{lll} \mathrm{B} + h\nu \longrightarrow \mathrm{B}^* & \alpha I & (1) \\ \mathrm{B}^* \longrightarrow \mathrm{B} + h\nu'_{\mathrm{F}} & k_1[\mathrm{B}^*] & (2) \\ \mathrm{B}^* \longrightarrow \mathrm{B} & k_2[\mathrm{B}^*] & (3) \\ \mathrm{B}^* + \mathrm{T} \longrightarrow \mathrm{B} + \mathrm{T}^* & k_3[\mathrm{B}^*][\mathrm{T}] & (4) \\ \mathrm{T} + h\nu \longrightarrow \mathrm{T}^* & \beta I & (5) \\ \mathrm{T}^* \longrightarrow \mathrm{T} + h\nu''_{\mathrm{F}} & k_4[\mathrm{T}^*] & (6) \\ \mathrm{T}^* \longrightarrow \mathrm{T} & k_5[\mathrm{T}^*] & (7) \end{array}$$

where I means the intensity of excitation absorbed by molecules per unit time and where α and β are the fractions of the absorption of benzene and toluene respectively. Namely, $\alpha=\varepsilon_{\mathrm{B}}[\mathrm{B}]/(\varepsilon_{\mathrm{T}}[\mathrm{T}]+\varepsilon_{\mathrm{B}}[\mathrm{B}])$ and $\beta=\varepsilon_{\mathrm{T}}[\mathrm{T}]/(\varepsilon_{\mathrm{T}}[\mathrm{T}]+\varepsilon_{\mathrm{B}}[\mathrm{B}])$, where ε stands for the absorption coefficient.

If the excitation is of a constant intensity and if the whole system is in equilibrium, we obtain:

$$[\mathrm{B}^*] = \alpha I/(k_1+k_2+k_3[\mathrm{T}]).$$

From Eq. (2) the fluorescence intensity per unit time of benzene is expressed as follows:

$$F_{\mathrm{B}} = k_1[\mathrm{B}^*] = k_1\alpha I/(k_1+k_2+k_3[\mathrm{T}]) = Q_{\mathrm{B}}\alpha I/(1+K[\mathrm{T}]).$$

Q_{B} and K are defined by the following relations;

$$Q_{\mathrm{B}} = k_1/(k_1+k_2) \text{ and } K = k_3/(k_1+k_2).$$

Similarly, we obtain for toluene:

$$F_{\mathrm{T}} = k_4[\mathrm{T}^*] = Q_{\mathrm{T}}I\{\beta+K[\mathrm{T}](\alpha+\beta)\}/(1+K[\mathrm{T}]).$$

If $\varepsilon_{\mathrm{T}}\approx\varepsilon_{\mathrm{B}}$ and $Q_{\mathrm{T}}\approx Q_{\mathrm{B}}$, we obtain:

$$\begin{aligned} F_{\mathrm{T}}/F_{\mathrm{B}} &= Q_{\mathrm{T}}(\beta+K[\mathrm{T}])/\alpha Q_{\mathrm{B}} \\ &= \{[\mathrm{T}]+K[\mathrm{T}]([\mathrm{T}]+[\mathrm{B}])\}/[\mathrm{B}]. \end{aligned}$$

Therefore, we obtain:

$$K = (F_{\mathrm{T}}/F_{\mathrm{B}})[\mathrm{B}]/[\mathrm{T}]([\mathrm{T}]+[\mathrm{B}]) - 1/([\mathrm{T}]+[\mathrm{B}]).$$

According to Robinson and Frosch,[4]

$$k_1 = 1.5 \times 10^6\ \mathrm{sec}^{-1},$$

we obtain from this definition:

$$k_2/k_1 = (1-Q_{\mathrm{B}})/Q_{\mathrm{B}}.$$

According to Lim,[5]

$$Q_{\mathrm{B}} = 0.2 \text{ in EPA at } 77^\circ\mathrm{K}.$$

If we use his data in our case, we obtain:

$$k_1 + k_2 = 5k_1 = 7.5 \times 10^6\ \mathrm{sec}^{-1}.$$

The $F_{\mathrm{T}}/F_{\mathrm{B}}$ ratio was estimated from the total fluorescence intensities of toluene and benzene, which were themselves derived from the fractional intensities of the key bands, of 0—623 of toluene and 0—992 of benzene, relative to the total intensities of toluene and benzene respectively. The results are shown in Table 3.

TABLE 3. RATE OF ENERGY TRANSFER FROM BENZENE TO TOLUENE AT VARIOUS CONCENTRATIONS

Toluene in benzene (mol/l)	$F_{\mathrm{T}}/F_{\mathrm{B}}$	k_3 (mol^{-1} sec^{-1})
10^{-4}	5.4×10^{-1}	4.1×10^{10}
5×10^{-4}	1.3	2.0×10^{10}
10^{-3}	2.1	1.6×10^{10}
5×10^{-3}	2.7	4.1×10^{9}
10^{-2}	9.5	7.1×10^{9}

Colson, Kopelman, and Robinson[6] studied the selection rules of the Frenkel exciton for the $k=0$ transition in molecular crystal. They assumed the $g\leftrightarrow u$ selection rule. We photographed the fluorescence spectrum of the benzene crystal at 90°K and found the very weak 0–404 band at 37400 cm^{-1}. It is believed that this experimental evidence provides important information for discussing the intermolecular interactions of the molecular crystal.

Pesteil and Zmerli[7] reported two phosphorescence spectra from benzene crystal at 20°K and ascribed them to the 1st and 2nd triplet–ground state transitions. We checked their spectra in detail and assumed that their spectra might be due to some impurity in benzene since the analysis looked too artificial to be understood. They placed the 0–0 bands at unobserved positions at 30574 cm^{-1} and 38724 cm^{-1} and analyzed the spectra of the 1st and 2nd transitions respectively. We studied the phosphorescence and fluorescence spectra of toluene of 10^{-3} mol/l in benzene at 4.2°K and 77°K and found that they coincided with the spectra of the 1st and 2nd transitions respectively, as established by Pesteil and Zmerli. The phosphorescence spectrum of toluene in benzene was observed at 4.2°K, but it could not be observed at 77°K.

The band at 28985 cm^{-1} was taken as the 0–0 band, and vibrational frequencies of 225, 226, 450, 622, 699, 795, 988, 1174, 1586, and 1609 cm^{-1} were found. They corresponded to the Raman frequencies[8] of 216($\mathrm{b_2}$), 216×2, 623($\mathrm{b_1}$), 695($\mathrm{b_2}$), 786($\mathrm{a_1}$), 1004($\mathrm{a_1}$), 1177($\mathrm{a_1}$), 1585($\mathrm{b_1}$), and 1604($\mathrm{a_1}$) cm^{-1} respectively. The fluorescence spectrum was observed even at 77°K and 90°K, as has been described previously. Pesteil[9] has also published a paper concerning Wannier exciton bands. The absorption band at 37112 cm^{-1} of the benzene crystal in his Fig. 4 must be ascribed to the 0–0 band of toluene. By the way, a similar explanation may be given for the band at 31061 cm^{-1} of the naphthalene crystal in his Fig. 6, which is to be ascribed to the 0–0 band of β-methylnaphthalene.

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