

크실렌과 요오드 사이의 전하이동 착물에 대한 압력과 온도의 영향

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The Effect of Pressure and Temperature on the Xylene-Iodine Charge Transfer Complex in *n*-Hexane

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요 약. *p*-크실렌과 요오드 사이의 전하이동착물의 안정도에 미치는 압력과 온도의 영향을 *n*-헥산용액에서 자외선 분광광도법으로 연구하였다. 압력은 1에서 1,600 bar, 온도는 25, 40, 60°C 사이에서 측정하였다. 착물의 평형상수는 압력 및 온도의 증가와 더불어 증가 및 감소하고 흡수계수는 대체로 증가함을 알았다. 이들 각 평형상수로부터 착물형성에 따른 부피, 엔탈피, 자유에너지 및 엔트로피 변화 양을 구하였다. 또한 압력의 증가에 의한 red-shift, 온도의 증가에 의한 blue-shift 현상 및 압력변화에 의한 진동자 세기와의 관계를 열역학적 함수와 관계지워 설명하였다.

ABSTRACT. The effect of pressures and temperatures on the stabilities of the *p*-xylene-iodine charge transfer complex have been investigated through ultraviolet spectrophotometric measurements in *n*-hexane. The stabilities of complexes were measured at 25, 40 and 60 °C under 1~1,600 bars.

The equilibrium constant of the complex was increased with pressure and decreased with temperature raising. The absorption coefficient was increased with both pressure and temperature. Changes of volume, enthalpy, free energy and entropy for the formation of complexes were obtained from the equilibrium constants. The red-shift observed a higher pressure, the blue-shift at a higher temperature and the relation between pressure and oscillator strength were discussed by means of thermodynamic functions.

INTRODUCTION

The basic theory of electron donor acceptor complexes has changed little since Mulliken's theory¹. According to this theory a small change in the separating distance of the two constituents in the complex should give rise to large changes in the formation constant *K* and the

electron transfer energy $h\nu$.² Thus a remarkable influence of hydrostatic pressure on the complexes might be expected.

Experimental work on the influence of pressure on charge transfer complexes has been reported by Ham³, Gott and Maisch⁴ and for solid complexes by Drickamer *et al.*^{5,6} and Offen *et al.*^{7,8} Mataga *et al.*⁹ have investiga-

ted the influence of pressure on the light absorption and fluorescence of *s*-tetracyanobenzene complexes. Recently Ewald^{10,11} has measured the effect of hydrostatic pressure on the formation constant *K* and the charge transfer absorption energy of donor-acceptor complexes in solution, and concluded that a large part of the effect could be explained by changes in the solvation of donors, acceptors and the complexes. Kwun¹² and Scholz¹³ has investigated charge transfer complexes in a wide temperature and density range and has discussed among others the problem of contact charge transfer complexes. Elevated pressure causes an increase of the charge transfer absorption, and, as a rule, gives rise to a red shift of the absorption. Blue shifts have been reported in exceptional cases for liquid solutions and for solids.^{4,13} A temperature increase causes a blue shift of the absorption band.

In the present work we have examined the effect of pressure and temperature on the formation of one to one CT-complexes with iodine of *p*-xylene (see xylene) in *n*-hexane.

We measured the absorbancy of their liquid solutions over a range of concentrations, pressures and temperatures and were able to evaluate *K*, ϵ and ΔG , ΔH , ΔS , Δv and *f*. From the change of *K* with pressure we have found the volume change ΔV which accompanies the formation of 1 mole of complex from its components. The red-shift observed a higher pressure, the blue-shift at a higher temperature and the relation between pressure and oscillator strength were discussed by means of thermodynamic functions.

EXPERIMENTAL

Materials. Samples of Merck Co. iodine (superpure grade), *p*-xylene (uvasol grade) and *n*-hexane (uvasol grade) were used without

purification.

Preparation of Stock Solution. The solution of iodine in *n*-hexane was prepared by weighing an appropriate quantity of iodine into a volumetric flask, and adding *n*-hexane solvent to make up to volume. The solution thus prepared was diluted further to suitable concentrations. The solutions of xylene in *n*-hexane was prepared by weighing an appropriate quantity of xylene into a volumetric flask and adding *n*-hexane to make up to volume. Each solution was freshly prepared at room temperature before making absorption spectrum measurements and wrapped with black paper to prevent any photochemical reaction in solution. The concentration of iodine was 4.45, 5.00, 6.00×10^{-4} mole·*l*⁻¹ and that of xylene was 1.02, 2.03, 3.04, 4.05×10^{-1} mole·*l*⁻¹. These were varied at least three fold for any one system. Both concentrations were adjusted so as to keep the absorbancy within suitable limits.

Apparatus. The spectra were measured on a Cary models 17H spectrophotometer modified to accommodate a high pressure cell. The apparatus has already been described in detail¹². A high pressure optical cell has been used with a spectrophotometer and with equipment to generate and to measure elevated pressure. It has two windows of synthetic colourless sapphire with a thin walled teflon cylinder between them which contains the solution. Using this arrangement the solution samples are in contact with sapphire and teflon only and thus a highly corrosive solution can be investigated. Spectra of xylene-iodine complex could be observed at high pressure without corrosion by iodine complex. The cell was kept at constant temperature by circulating water through it supplied by a thermostat. The external part of the cell was made of brass. The test solution was injected, using glass syring,

through a capillary into the high pressure cell which then connected to a high pressure apparatus.

The Spectrophotometric Measurements.

The absorbancies of stock solutions of iodine and xylene in *n*-hexane were measured over the region of wave lengths from 270 to 700 nm using the pure solvent, *n*-hexane, as the blank. Then, the stock solution of xylene was mixed at various ratios with the solution of the iodine. The absorbancies of the resulting solution were immediately measured. (The prolonged keeping of the mixture solutions was avoided as otherwise slow chemical changes might have occurred.) The blank in this case was the *n*-hexane solution of xylene with the same concentration as those of solutions containing iodine. High pressure optical cell was maintained at the desired temperatures 25, 40 and 60 °C, by a thermostat within ± 0.1 °C. The absorbancies of solution at the complex absorption maximum were usually determined in the neighborhood of 300 nm.

RESULTS AND DISCUSSION

A set of spectra of xylene-iodine CT-complexes in *n*-hexane at various pressures is shown in Fig. 1. The broad absorption bands are typical of EDAC in solution and one reason why quantitative determination of the absorption maximum is often difficult. When comparing spectra at different pressures and temperatures, it is necessary to allow for change in density of solution. In the present work, the various parameters are discussed individually.

Calculation of Equilibrium Constant for the CT-Complex Formation. The absorption spectra of the individual stock solution of iodine, or xylene in *n*-hexane did not indicate the presence of maximum absorption peaks in the vicinity of 300 nm. On the other hand, the

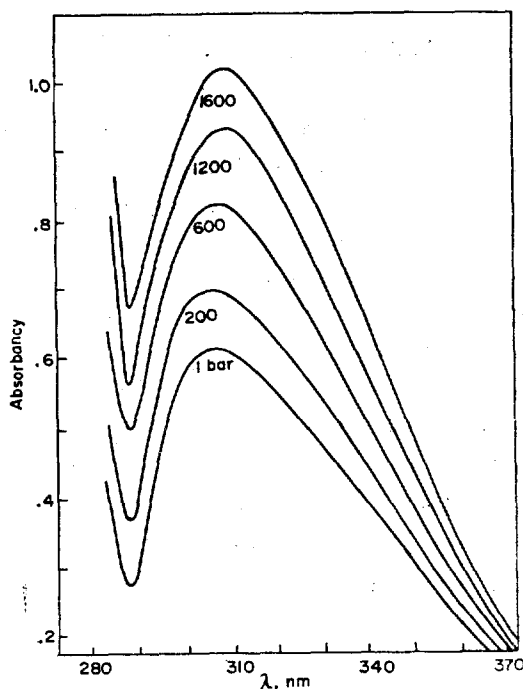


Fig. 1. Absorption spectrum for the system of xylene (0.405M) with iodine ($6.00 \times 10^{-4}M$) complex in *n*-hexane at various pressures (25°C).

absorption spectra of the solution of a mixture of xylene with iodine did indicate the presence of absorption maxima in the region of wave lengths near 300 nm. The maximum absorption observed is attributed to the formation of complexes of xylene with iodine in solution.

These complexes are assumed to be one to one molecular complexes of which was first proposed by Benesi and Hildebrand for the system of benzene-iodine in carbon tetrachloride¹⁵.



Where *D* denotes the donator molecules, *A* acceptor molecules and *C* the one to one molecular complex *D*·*A*. The equation of Benesi and Hildebrand has been modified for high pressures in order to calculate the equilibrium

constant K and the absorption coefficient ϵ , *i. e.*

$$\frac{[A]_0 \cdot d \cdot (\rho/\rho_0)}{\log(I_0/I)} = \frac{1}{K \cdot \epsilon} \cdot \frac{1}{[D]_0} + \frac{1}{\epsilon} \quad (2)$$

which is now in the form, $y=mx+b$. Where $[A]_0$ and $[D]_0$ are the initial molar concentration of acceptor and donor respectively, $\log(I_0/I)$ is absorbancy (A) at λ_{max} , d is the internal distance between the windows. It was always 1.06 cm. ρ_0 and ρ are densities of solution at 25 °C and 1 bar and at the temperature and pressure of experiment respectively. The values of the ratios ρ/ρ_0 for the solutions were derived from results of Kuss and Taslimi¹⁶. The values of the equilibrium constant K and absorption coefficient ϵ were found from equation (2). After the values of A were determined experimentally, the quantities of y term were plotted against x term. The plots indicated good linearity between the two quantities in all the system examined. Hence, the values of m and b term were calculated from the slopes and the intercept of the straight lines. The least square method was utilized to determine slopes and intercepts. Knowing the values of $1/(K \cdot \epsilon)$ and $1/\epsilon$, the value of K and ϵ were calculated. Since linearities were observed between y and x experimentally, it can be concluded that the assumption of the formation of one to one complexes should be correct.

The Xylene-Iodine CT-Complexes Formation. Data obtained at temperature 25, 40, 60 °C and pressure 1, 200, 600, 1200, 1,600 bar on the system of xylene with iodine in *n*-hexane. The data show a straight line relationship between y and x (Fig. 2).

These linearities indicate that the assumption of the formation of one to one molecular complex xylene-iodine is being correct as it was discussed previously¹⁵.

The results of the present study at 25 °C and

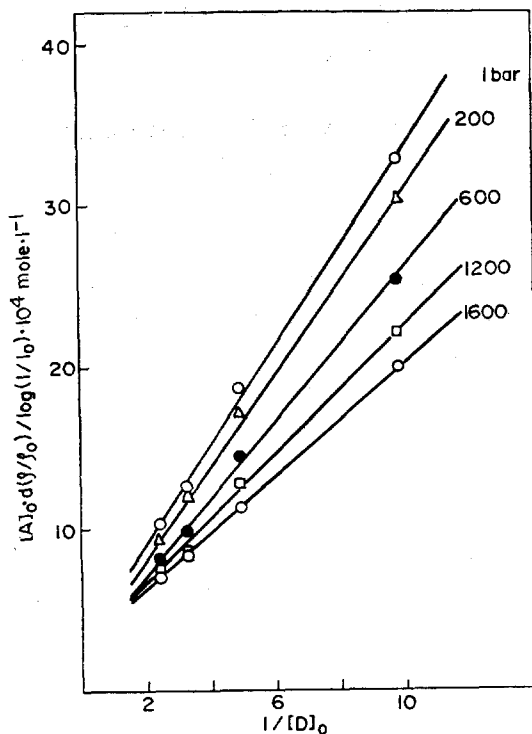


Fig. 2. Plot of $[A]_0 \cdot d \cdot (\rho/\rho_0) / \log(I_0/I)$ versus $1/[D]_0$ of the xylene-iodine system at various pressures (25°C).

1 atm are now compared with those reported in the literature. Keefer and Andrews¹⁷ reported an equilibrium constant value of 0.31 for the complex, *p*-xylene-iodine in carbon tetrachloride. And Ketelaar¹⁸ reported a value of 2.96 (as K_x) for complexes in *n*-hexane. The results of this study are similar to those of previous studies.

Equilibrium Constants, Absorption Coefficients and Volume Changes. The value of K and ϵ can be calculated directly only if they are obtained by fitting a linear equation (2). The equilibrium constants in molar concentration units and absorption coefficients are summarized in Table 1 where the results are presented showing the influence of temperature and pressure on K and ϵ . It can be seen that both K and ϵ increase with the pressure at the con-

Table 1. Absorption maxima, equilibrium constants, absorption coefficients and volume change of $C_6H_4(CH_3)_2I_2$ CT-complexes.

Temperature (°C)	Pressure (bar)	λ_{max} (nm)	K (l · mole ⁻¹)	ϵ (l · mole ⁻¹ · cm ⁻¹)	$-\Delta V$ (cm ³ · mole ⁻¹)
25	1	304.5	0.912	3,535	7.61
	200	306.0	0.996	3,534	
	600	307.2	1.07	4,016	
	1,200	308.5	1.17	4,172	
	1,600	309.5	1.57	4,178	
40	1	304.0	0.812	3,619	6.40
	200	305.5	0.883	3,548	
	600	306.6	0.902	3,980	
	1,200	307.7	0.988	4,225	
	1,600	308.2	1.28	4,236	
60	1	302.0	0.697	3,760	6.16
	200	302.8	0.740	3,762	
	600	303.7	0.755	4,251	
	1,200	304.5	0.832	4,583	
	1,600	305.2	1.07	4,564	

stant pressure, K decreases with temperature. On the other hand, ϵ increases with temperature.

We have found an increase in K and ϵ for the xylene-iodine complex at high pressure. These is a smaller increase in oscillator strength and thus indicating that the band width decreases at high pressure. The quantitative results differ from those of Gott and Maisch⁴.

The volume changes ΔV associated with the formation of CT-complexes from their components can be calculated from the equilibrium constants by the following equation

$$\frac{d \ln K}{dp} = -\frac{\Delta V}{RT} \quad (3)$$

and are given by the slopes of lines as shown in Fig. 3. The volume changes associated with formation of the CT-complexes, and their absorption maxima are given in Table 1.

In studying the influence of pressure and temperature on λ_{max} , it was found that a red-shift or a blue-shift takes place depending on

whether the pressure or temperature increase. Such behaviour was also reported by Ewald.^{10,11} Also the volume change ΔV was found to decrease with increasing temperature. The decrease in component separation caused by compression will be small compared with the difference between the sum of the van der Waals radii and the CT band length and will not be reflected in the observed ΔV . The measured values of ΔV represent the change in volume when the complex is formed from its components.

The structures of some complexes are known in the solid state from the X-ray diffraction work of Wallwork¹⁹. One can calculate the volume change associated with the formation of the complexes from their components by using Wallwork's distances and van der Waals radii to calculate the van der Waals volumes of both the separate components and the complexes. The general agreement of ΔV calculated from the structure of the solid complex and

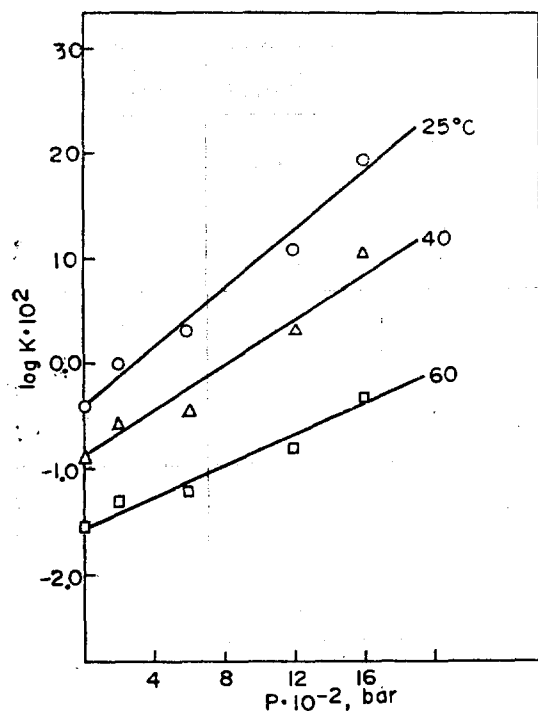


Fig. 3. Pressure dependence of $\log K$ for the xylene-iodine system at several temperatures.

the measurements in solution is consistent with the assumption that similar complexes are formed in the two cases. The magnitude of ΔV is connected with the magnitude of K , but exceptionally large values of ΔV can occur where steric effects prevent the formation of a complex.

Thermodynamic Functions. The value of free energy, enthalpy and entropy of complex formation was calculated from the equilibrium constant.

Good linearity was obtained from the plots of the $\log K$ vs. $100/T$ (Fig. 4). From the slope the enthalpy of the complex formation ΔH was calculated. Then for each temperature the free energy of the complex formation ΔG and entropy of that ΔS was calculated. The results obtained are summarized in Table 2.

The values of ΔH and ΔS have been calculated

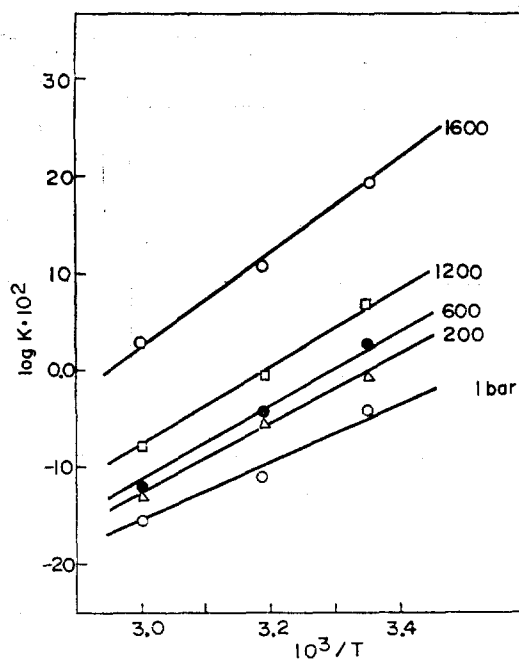


Fig. 4. Temperature dependence of $\log K$ for the xylene-iodine system at various pressures.

from experimental results at 1 bar and found similar to the values reported by Ketelaar¹⁸. Although the accuracy of the data is not great they show a definite increase of ΔH and ΔS with pressure. There is an increase in oscillator strength at high pressure which is paralleled by the increases in ϵ_{\max} . And hence there is no increase in bandwidths.

Pressure, Temperature Shift and Oscillator Strength. The CT-bands are characteristically broad and thus the ν_{\max} were estimated by taking the mean of the maxima of all the measurement on a particular system.

The oscillator strength f of the CT-absorption could be evaluated directly by graphical method on a wave number scale. Its value was estimated from $\epsilon_{\max} \Delta \bar{\nu}_{1/2}$, using the equation²⁰

$$f = 4.319 \times 10^{-9} \epsilon_{\max} \Delta \bar{\nu}_{1/2} = 10.36 \times 10^{-9} \times \epsilon_{\max} (\nu_{\max} - \nu_{1/2} L) \quad (4)$$

Table 2. Thermodynamic functions^a of $C_6H_4(CH_3)_2I_2$ CT-complex at various pressures.

Temp. (°C)	Pressure (bar)														
	1			200			600			1,200			1,600		
	$-\Delta H$	ΔG	$-\Delta S$	$-\Delta H$	ΔG	$-\Delta S$	$-\Delta H$	ΔG	$-\Delta S$	$-\Delta H$	ΔG	$-\Delta S$	$-\Delta H$	ΔG	$-\Delta S$
25	54.6	5.31		2.38	5.46		-40.1	6.46		-93.0	6.14		-267	6.40	
40	1,528	130	5.29	1,627	77.4	5.44	1,966	64.2	6.48	1,922	7.51	6.16	2,178	-154	6.46
60	239	5.30		199	5.48		186	6.46		122	6.14		-44.8	6.40	

^a ΔH , ΔG in cal · mole⁻¹, ΔS in cal · mole⁻¹ · deg⁻¹.Table 3. Pressure and temperature shift^a of $C_6H_4(CH_3)_2I_2$ CT-absorption maxima and oscillator strength of $C_6H_4(CH_3)_2I_2$ CT-bands

Temperature (°C)	Pressure (bar)	$\Delta\nu$ (cm ⁻¹)	$\Delta\nu'$ (cm ⁻¹)	$f \cdot 10^2$
25	1			19.7
	200	160		19.6
	600	288		20.0
	1,200	425		20.1
	1,600	530		20.4
40	1		55.1	21.4
	200	162	53.5	21.6
	600	279	63.7	21.4
	1,200	395	84.3	21.8
	1,600	448	136	22.2
60	1		273	23.0
	200	88.1	345	23.5
	600	185	375	24.1
	1,200	347	426	24.4
	1,600	454	455	24.6

^a Red shift ($\Delta\nu$) with increasing pressure ($\nu_1 - \nu_p$)_{max}, blue shift ($\Delta\nu'$) with increasing temperature ($\nu_1 - \nu_{25}$)_{max}.

Where $\Delta\nu_{1/2}$ is the band which at $\epsilon = \epsilon_{\max}/2$ and $\nu_{1/2L}$ is the half-height frequency at the red side of the maximum of the CT-band. The shifts of absorption maxima and the value of oscillator strength observed at various pressure are shown in Table 3. Ewald^{10,11}, Kwun¹² and Scholz¹³ have reported similar shifts.

The dependence of oscillator strength on pressure for various temperatures is generally

not significant, although it increases slightly with temperature. Further, it was found that its dependence on temperature is rather significant for a given pressure. The oscillator strength shows a linear increase with pressure up to 1,600 bars (Fig. 5), $\partial f/\partial P$ is 4.83, 5.03, $9.85 \cdot 10^{-6} \text{ bar}^{-1}$ at 25, 40, and 60°C respectively.

It can be seen that the red-shift increases with pressure but not significantly with temperature. The dependence of red shift on pressure for a given temperature would indicate a low energy for complex formation (see Table 2). Further results are shown where it can be seen that the blue shift is increasing with the temperature under a given pressure. Also, the shift increases with pressure at a given temperature.

The xylene-iodine system in *n*-hexane solution can be compared with the toluene-iodine system in *n*-hexane investigated by Kwun¹² at temperatures of 25, 40, and 60°C and pressures of 1, 200, 600, 1,200, and 1,600 bars. The main properties are similar in both systems. Complex formation is markedly stronger, however, in the xylene system. A similarity exists in the temperature dependence of ΔV . For toluene-iodine $\partial \Delta V/\partial T$ is positive, also it is positive for xylene-iodine.

Attempts are described in the literature for correlating the electron transfer energy $h\nu_{\max}$ to

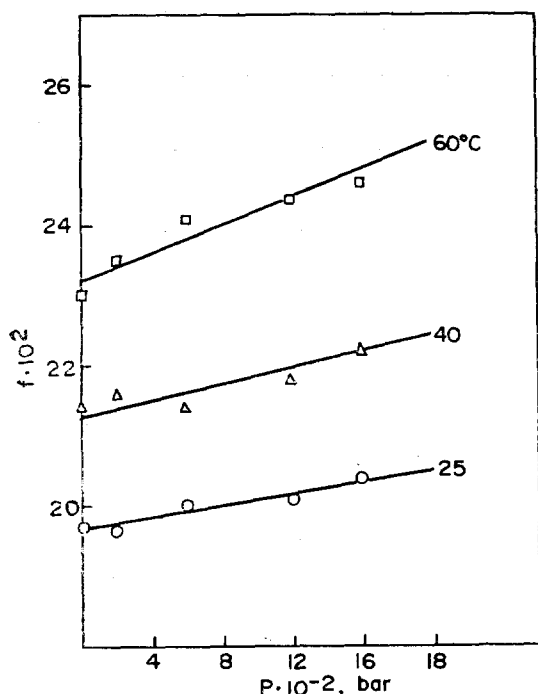


Fig. 5. Pressure dependence of oscillator strength for the xylene-iodine system at several temperatures.

ΔG values of complex formation. Briegleb²¹ reported an almost linear relationship between the quantities for the series of successively methylated benzene molecules.

The red shift of the band maximum at different pressures (Table 3) are plotted as a function of the respective change of ΔG (Table 2). For the pressure variation a straight line results.

An interpretation of the expressions depends on the model used for charge transfer complexes. If one supposes as in reference¹¹ that the variation at the depth of potential in the ground state is described by ΔG , then the numerical factors in the equation should give information about the shift or deformation of the potential of the excited state.

Apparently, the observed shift is a balance between the red-shift due to decreased separa-

tion in the ground state, and a blue-shift due to the lowering of the ground state energy by increased resonance between the no-bond and the dative bond structure, as suggested by Offen and Abidi²².

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