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Photoisomerization and Tunneling Isomerization of Tetrachlorohydroquinone in a Low-Temperature Argon Matrix

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Torsional isomerization of tetrachlorohydroquinone in a low-temperature argon matrix has been investigated by Fourier transform infrared spectroscopy with the aid of density-functional-theory calculations. Infrared bands of the more stable isomer, trans, were observed in an argon matrix at 16 K. Those of the less stable isomer, cis, were observed during UV irradiation but disappeared immediately after the irradiation was discontinued. The isomerization from trans to cis occurred in the dark despite the high torsional barrier, 19.1 kJ mol^{-1}, when the matrix temperature was increased from 16 to 30 K. The enthalpy difference between the two isomers was estimated from the observed population changes to be 0.46 ± 0.10 kJ mol^{-1} (39 ± 8 cm^{-1}) by a least-squares fitting. This isomerization in low-temperature matrixes is ascribed to the matrix-induced hydrogen-atom tunneling.

Introduction

In low-temperature rare-gas matrix-isolation experiments, the population ratio between some isomers at a deposition-nozzle temperature can be maintained in matrixes.[1] For example, the population ratio between gauche and trans of 1,2-dichloroethane was examined at various temperatures of a deposition nozzle, with the result that the enthalpy difference estimated from the population changes corresponds to the values obtained by other experimental methods. Then, it was confirmed that the population ratio at the deposition-nozzle temperature can be certainly maintained in low-temperature rare-gas matrixes. Furthermore, less stable isomers produced by irradiation in low-temperature matrixes do not return to their original structures after stopping the irradiation, when the isomerization barrier is high enough to inhibit thermodynamical isomerization over the barrier.[2,3] A lot of spectroscopic data for less stable isomers photoproduced from more stable isomers have been obtained by the matrix-isolation technique.[2−7]

However, we recently found that the torsional isomerization of hydroquinone (HYQ) and its related compounds in low-temperature matrixes occurs reversibly in the dark as if the isomerization barrier were negligible. To explain this phenomenon, we proposed a hydrogen-atom tunneling effect.[8,9] Similar isomerizations due to tunneling effect in matrixes have also been reported,[10−12] but no essential understanding has been given.

The energy difference between cis and trans of HYQ is smaller than 1 kJ mol^{-1} in the gas phase, and the potential surface of the OH torsional mode has an asymmetric double minimum.[13−15] Therefore, the tunneling isomerization between cis and trans is basically difficult.[13] In the matrix, however, the energy difference becomes nearly equal to zero by interaction with matrix atoms; the potential energy surface can be treated as a quasi-equivalent double minimum one. If the energy of the OH torsional vibrational levels for cis corresponds to that for trans, the tunneling isomerization for HYQ in low-temperature rare-gas matrixes should be possible. A schematic explanation for the tunneling isomerization is given in Figure 1. However, we could not completely exclude the possibility that the isomerization barrier for HYQ is lowered less than 4 kJ mol^{-1} by the interaction between HYQ and matrix atoms. If this is true, thermodynamical isomerization over the barrier might occur.[16]

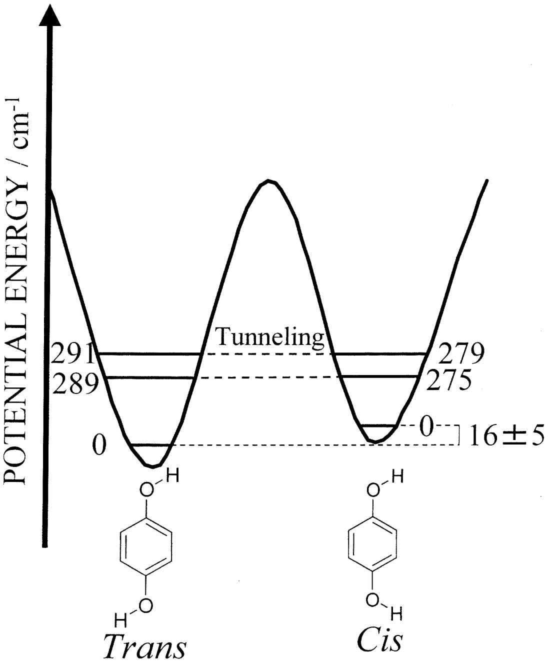

Figure 1. Schematic potential energy surface of hydroquinone isolated in matrixes:[8] Torsional vibrational levels are assumed to be a tunneling pathway.

In the present work, we have performed similar experiments for tetrachlorohydroquinone (TCHYQ), which has two stable isomers such as HYQ, trans and cis, as shown in Figure 2. Both isomers of TCHYQ seem to be stabilized more strongly than those of HYQ by two intramolecular hydrogen bondings

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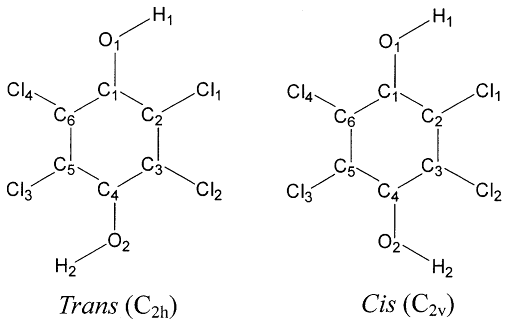

Figure 2. Two possible isomers of tetrachlorohydroquinone: Numbering of atoms is given.

between hydrogen and chlorine atoms, resulting in a torsional barrier higher than that of HYQ. In this case, thermodynamical isomerization over the barrier is clearly impossible, despite a slight lowering of the barrier caused by the interaction with matrix atoms. A comparison of the results of TCHYQ and HYQ has led us confirm that the torsional isomerization originates from the matrix-induced hydrogen-atom tunneling.

Experimental and Calculation Methods

TCHYQ was purchased form Avocado Research Chemicals Ltd. Since the vapor pressure of TCHYQ was too low to transfer the vapor sufficiently into a glass cylinder, a small amount of the solid was placed in a stainless steel nozzle with a heating system, on which pure argon gas (Nippon Sanso, 99.9999% purity) was flowed. The sample was heated to about 320 K, and the flow rate of argon gas was experimentally adjusted to obtain sufficient isolation. The mixed gas was expanded through a stainless steel pipe (a diameter of 1/16 in.) and deposited in a vacuum chamber on a CsI plate cooled by a closed-cycle helium refrigerator (CTI Cryogenics, model M-22) to about 16 K. The CsI plate was shielded from thermal radiation from its surroundings. The temperature of the CsI plate was controlled by a thermostabilizer (IWATANI, TCU-4) with a PID (Proportional plus Integral plus Derivative) action and stabilized within an error of 0.1 K. UV light from a superhigh-pressure mercury lamp was used to induce photoisomerization, where a water filter and a U330 band-pass filter (HOYA) were used to remove thermal reactions and to select irradiation wavelength, respectively. Infrared spectra of the matrix samples were measured with an FTIR spectrophotometer (JEOL, model JIR-7000). The spectral resolution was 0.5 cm^{-1}, and the number of accumulation was 64. Other experimental details were reported elsewhere.[17,18]

Density-functional-theory (DFT) calculations were performed by using the GAUSSIAN 98 program[19] with the 6-31++G** basis set. Becke's three-parameter hybrid density functional,[20] in combination with the Lee–Yang–Parr correlation functional (B3LYP),[21] was used to optimize the geometrical structures and vibrational wavenumbers.

Results and Discussion

Conformation of TCHYQ. TCHYQ has two possible isomers as shown in Figure 2. The energy difference between the more stable isomer, trans, and the less stable isomer, cis, is estimated to be 1.56 kJ mol^{-1} by the DFT calculation, while the isomerization barrier scaled from the potential minimum of trans is 19.1 kJ mol^{-1}. One OH bond in the transition state is perpendicular to the plane of the benzene ring. Both isomers are stabilized by two sets of intramolecular hydrogen bonding between hydrogen and chlorine atoms, resulting in that the torsional barrier, 19.1 kJ mol^{-1}, is higher than that of HYQ, 10.8 kJ mol^{-1}.[8] Due to the bonding, the H···Cl lengths, calculated to be 2.380 and 2.395 Å for trans and cis, respectively, are clearly shorter than the sum of the van der Waals radii of hydrogen and chlorine atoms, 2.479 Å. Since the H···Cl length of trans is shorter than that of cis, trans may be stabilized more strongly by the hydrogen bonding. Other bond lengths for trans and cis are found to be consistent with each other within 0.003 Å, as shown in Table 1. No molecular-orbital calculations on this molecule have been published to our knowledge.

TABLE 1: Optimized Geometrical Parameters of Trans and Cis Isomers of Tetrachlorohydroquinone Obtained at the DFT/B3LYP/6-31++G Level**

parameter[a]	trans	cis
	bond length (in Å)	
O_1-H_1	0.970	0.970
C_1-O_1	1.354	1.354
C_2-Cl_1	1.749	1.749
C_3-Cl_2	1.736	
C_5-Cl_3		1.735
$H_1\cdots Cl_1$	2.380	2.395
C_1-C_2	1.404	1.401
C_2-C_3	1.399	1.400
C_3-C_4	1.403	
C_4-C_5		1.406
	bond angle (in deg)	
$C_1-O_1-H_1$	109.3	109.5
$C_2-C_1-O_1$	122.9	122.9
$C_6-C_1-O_1$	118.3	118.3
$C_1-C_2-Cl_1$	117.5	118.0
$C_3-C_2-Cl_1$	121.1	121.2
$C_2-C_3-Cl_2$	121.4	
$C_4-C_3-Cl_2$	118.8	
$C_4-C_5-Cl_3$		118.2
$C_6-C_5-Cl_3$		121.2

[a] Numbering of atoms is given in Figure 2.

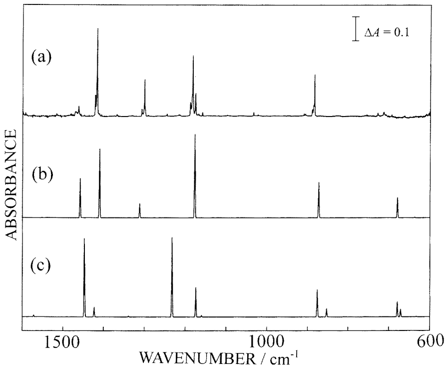

Figure 3. Infrared spectrum of tetrachlorohydroquinone: (a) Observed spectrum in Ar matrix at 16 K. (b, c) Calculated spectral patterns of trans and cis, respectively, obtained by DFT/B3LYP/6-31++G** using a scaling factor of 0.98.

Infrared Spectrum of TCHYQ in a Matrix. According to the Boltzmann distribution law, the population ratio of cis/trans is calculated to be 0.57 at the deposition-nozzle temperature, 320 K. As described in the introduction, an infrared spectrum based on the population ratio should be observed in a low-temperature matrix. Figure 3 shows an infrared spectrum of TCHYQ in an argon matrix at 16 K with the calculated spectral patterns of cis and trans. All the calculated wavenumbers are scaled by a factor of 0.98.[22] By comparing the observed spectrum with the two spectral patterns, the observed bands are assigned to trans only. Although the band appearing at 1176 cm^{-1} seems to be assignable to cis, no other bands for cis are observed in the spectrum. Thus, we conclude that the 1176 cm^{-1}

TABLE 2: Observed and Calculated Vibrational Wavenumbers (in cm^{-1}) and Their Relative Infrared Intensities of *trans*-Tetrachlorohydroquinone in an Argon Matrix at 16 K

obsd		calcd		
ν	int	ν^a	int	sym
		3683	0	a_g
3549	54.1	3681	56.2	b_u
		1588	0	a_g
		1570	0	a_g
1462^b	8.6	1458	47.5	b_u
1417^b	100	1410	82.3	b_u
		1342	0	a_g
1301^b	44.2	1312	17.3	b_u
		1233	0	a_g
1182^b	69.2	1177	100	b_u
1159	3.8	1160	0.2	b_u
1034^c	3.9			
		1014	0	a_g
884^b	49.0	873	42.9	b_u
		856	0	a_g
729^c	3.2			
713	3.4	679	24.2	b_u
694	3.1			
662	2.2	672	0	a_g
		637	0.7	a_u
		576	0	b_g
		520	2.5	a_u
		489	0	a_g
		436	0.2	b_u
		394	0	b_g
		388	50.8	a_u
		358	0	b_g
		341	0	a_g
		336	5.5	b_u
		326	0	a_g
		318	0	b_g
		284	0	a_g
		215	0.0	b_u
		207	0.0	b_u
		200	0	a_g
		185	0.1	a_u
		119	0	b_g
		95	0.0	a_u
		71	0.0	a_u

[a] A scaling factor of 0.98 is used. [b] Bands exhibiting splitting. [c] Assigned to combination modes.

band, which is inconsistent with any cis bands shown later, is due to the Fermi resonance with the strong 1182 cm^{-1} band or a combination band. The observed and calculated wavenumbers of trans are summarized in Table 2. The intensities of the 1462 and 713 cm^{-1} bands are slightly inconsistent with the corresponding calculated values for the 1458 and 679 cm^{-1} bands. It is known that consistency between observation and calculation for molecules including multiple chlorine atoms is slightly worse than that for other molecules.[22,23] Other weak bands are assignable to combination modes with the intense O−H torsional mode, 388 cm^{-1}.

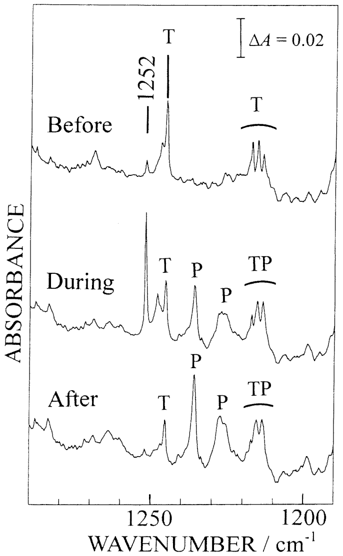

Figure 4. Infrared spectra of tetrachlorohydoquinone measured before, during, and after UV irradiation: Bands marked with T and P represent trans and a photoproduct, respectively.

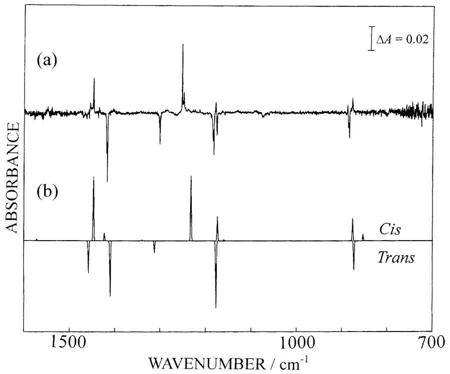

Figure 5. Difference spectrum (a) between those measured before and during UV irradiation, where the bands of photoproducts are subtracted. (b) Calculated spectral pattern obtained by the DFT/B3LYP/6-31++G** using a scaling factor of 0.98; cis is upside, and trans is downside.

Infrared Spectrum of Transient Species. After measurement of Figure 3, the matrix sample was irradiated by UV light to observe isomerization from trans to cis. The spectral region between 1290 and 1190 cm^{-1} is expanded by about 40 times in Figure 4, where the trans bands appearing at 1246 and 1216 cm^{-1} with splittings are due to combination mode. New bands of unknown photoproducts are observed at 1215, 1228, and 1237 cm^{-1} in the spectrum measured after the irradiation. On the other hand, infrared bands of a transient species are observed during UV irradiation with those of the photoproducts. For example, the band at 1252 cm^{-1}, which cannot be assigned to either trans or the photoproduct, appears strongly during the UV irradiation through a U330 band-pass filter and disappears immediately after the irradiation was discontinued. Figure 5a shows a difference spectrum obtained by subtraction of the infrared bands of the unknown photoproducts, while Figure 5b shows calculated spectral patterns of both isomers. The calculated spectral pattern satisfactorily reproduces the observed difference spectrum. Thus, we conclude that the transient species is identified to cis. The observed and calculated wavenumbers of cis are summarized in Table 3 with their relative intensities and vibrational modes. Similar phenomena that the less stable isomer produced during UV irradiation returns to the more stable isomer immediately after termination of the irradiation have been observed for HYQ[8] and chloranilic acid.[9]

Enthalpy Difference between *cis* and *trans*. As shown in Figure 6, the intensity of the 1252 cm^{-1} band, which is assigned to cis in the previous section, increases as the matrix temperature increases. The intensity changes are found to be reversible in the matrix-temperature range between 16 and 30 K. The cis/trans population ratio depends on the matrix temperature, as plotted in Figure 7. The relationship between the inverse of the matrix temperature and ln (A_{cis}/A_{trans}), where A_{cis} and A_{trans} represent the absorbances of cis (1252 cm^{-1}) and trans (1246 cm^{-1}), is found to be approximately linear in this temperature range. The enthalpy difference between cis and trans is estimated

TABLE 3: Observed and Calculated Vibrational Wavenumbers (in cm^{-1}) and Their Relative Infrared Intensities of *cis*-Tetrachlorohydroquinone

obsd[a]		calcd		
ν	int	ν^b	int	sym
3558	17.9	3689	32.7	a_1
3555	28.2	3687	22.3	b_2
		1585	0.4	a_1
		1572	2.3	b_2
1447	51.3	1447	98.7	b_2
1435	7.2	1423	12.1	a_1
		1339	1.3	a_1
		1312	0.3	a_1
1252[c]	100	1232	100	b_2
1178[d]	15.6	1174	37.3	a_1
		1160	1.9	b_2
		1013	0.4	a_1
888[d]	10.2	876	34.3	b_2
877	23.1	853	10.3	b_2
		679	18.6	a_1
		671	9.3	b_2
		633	0.6	b_1
		588	0.0	b_2
		489	0.0	a_1
		466	0.0	a_2
		436	0.2	b_2
		384	54.6	b_1
		376	0.0	a_2
		341	0.0	a_1
		337	0.0	a_2
		335	1.1	a_1
		326	0.7	b_2
		319	1.2	b_1
		282	2.4	b_2
		211	0.0	a_1
		210	0.0	b_2
		200	0.0	a_1
		18	0.1	b_1
		117	0.0	a_2
		95	0.0	b_1
		71	0.0	a_2

[a] Observed during UV irradiation. See text. [b] A scaling factor of 0.98 is used. [c] Bands exhibiting splitting. [d] Overlapped with trans bands.

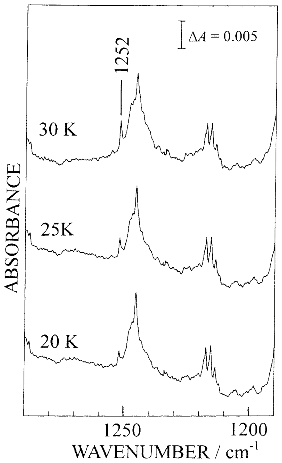

Figure 6. Reversible spectral changes of tetrachlorohydroquinone in Ar matrix at various matrix temperatures.

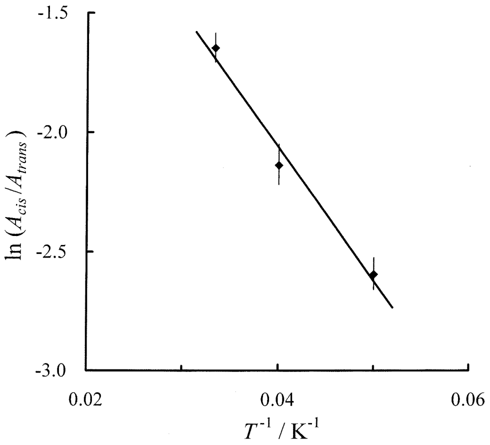

Figure 7. Logarithmic plot of absorbance ratio versus inverse of matrix temperature: A_{cis} and A_{trans} represent the absorbances of cis (1252 cm^{-1}) and trans (1246 cm^{-1}), respectively. Error bars represent uncertainties in peak area measurements. Solid line represents the values calculated by a least-squares fitting.

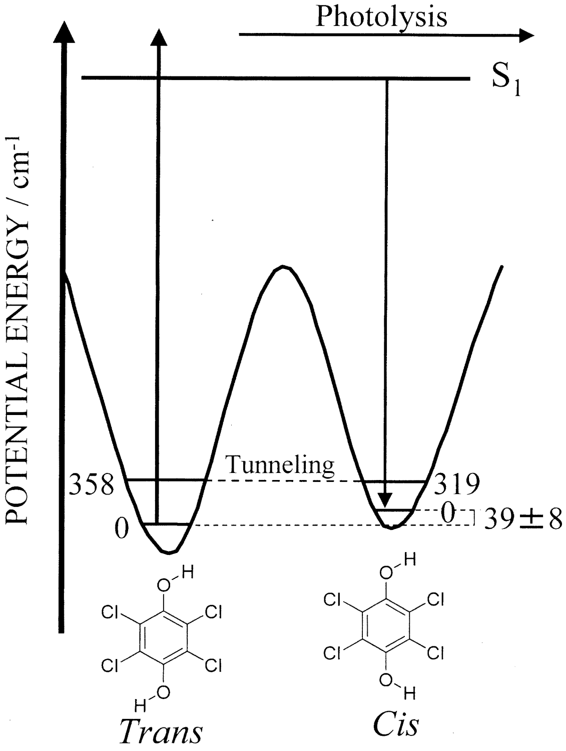

Figure 8. Schematic potential energy surface of tetrachlorohydroquinone isolated in an argon matrix: Torsional vibrational energy levels are calculated by the DFT/B3LYP/6-31++G**. The zero-point vibration energy difference between cis and trans, 39 ± 8 cm^{-1}, is estimated from the spectral change observed at various matrix temperatures.

to be 0.46 ± 0.10 kJ mol^{-1} (39 ± 8 cm^{-1}) by a least-squares fitting. The experimental enthalpy difference is closer to zero than the calculated zero-point energy difference, 0.99 kJ mol^{-1}, which is obtained from the calculated energy difference, 1.56 kJ mol^{-1}, by the zero-point-energy correction. This fact may be explained in terms of dipole-moment interaction with the matrix atoms, where the less stable isomer, cis, is more stabilized than the more stable isomer, trans, because the former is polar and the latter is nonpolar. A similar phenomenon is observed in the case of HYQ, where the estimated enthalpy difference, 0.19 kJ mol^{-1}, is smaller than that obtained by the DFT calculation, 0.50 kJ mol^{-1}.[8]

Thermal Isomerization over the Barrier or Tunneling Isomerization through the Barrier? There are two possible mechanisms to induce the isomerization in low-temperature matrixes in the dark, as described in detail in our previous papers.[8,9] One is quantum tunneling effect through the barrier and the other is thermodynamical process over the barrier. It is known that the latter is basically difficult in matrixes at 15 K when the barrier is higher than 4 kJ mol^{-1}.[16] For example, the torsional barrier heights for 1,3,5-benzenetriol[24] and 3-chlorophenol[22] are calculated to be 17.6 and 15.6 kJ mol^{-1}, respectively, by the same DFT/B3LYP/6-31++G** method, and their thermal isomerization is inhibited in low-temperature matrixes. Since the calculated barriers for TCHYQ and HYQ are higher than 10 kJ mol^{-1}, thermal isomerization over the barrier is ruled out especially for TCHYQ, whose barrier height is calculated to be 19.1 kJ mol^{-1}. We conclude that our observation is tunneling isomerization through the barrier instead of thermal isomerization over the barrier.

One may wonder which energy level plays a role for tunneling on the asymmetric potential surface. In the case of HYQ in a xenon matrix, the enthalpy difference, 16 ± 5 cm^{-1}, almost corresponds to the energy difference of the OH torsional vibrations: 291 and 289 cm^{-1} for trans and 279 and 275 cm^{-1} for cis. Then, we concluded that the cis−trans isomerization for HYQ occurs through the OH torsional vibrational levels by tunneling, as shown in Figure 1. In the case of TCHYQ, the energy levels of the vibrational modes relating to the torsional motions are calculated to be 358 and 319 cm^{-1} for trans and cis, respectively, after scaling. The vibrational energy difference, 39 cm^{-1}, corresponds to the enthalpy difference, 39 ± 8 cm^{-1}, derived from the population changes at various matrix temperatures. Then, we conclude that these vibrational energy levels play a role for tunneling in the low-temperature matrix state. A schematic potential diagram to express the tunneling isomerization is given in Figure 8.

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