lowing characteristics which are common for simple sensitization processes. As shown in Figure 6, the redox potential of $\operatorname{Ru}(\operatorname{bpy})_3^{3+}/\operatorname{Ru}(\operatorname{bpy})_3^{2+}$ is located higher than the valence band of TiO_2 . It means that the oxidation power of $\operatorname{Ru}(\operatorname{bpy})_3^{3+}$ is weaker than that of the holes in the valence band of TiO₂. Thus, oxidation of methanol-water by visible irradiation of $Ru(bpy)_3^{2+}/TiO_2$ may be more difficult than the oxidation by direct excitation of TiO_2 . This increases the probability of the recombination process. Furthermore, the band bending of TiO_2 is considered to be small under conditions of hydrogen evolution, and this is also unfavorable for charge separation of injected electrons.

Conclusion

We have obtained time-resolved luminescence spectra of $Ru(bpy)_{3}^{2+}$ which have characteristic features depending on the interaction on the surfaces. Although the decay characteristics are not so simple as we had expected, the origin of more than two decay components of different lifetimes would be mainly assigned to different electrontransfer rates depending on the relative position of Ru- $(bpy)_{3}^{2+}$ on the solid surface. The concentration quenching and the electron and energy transfer to the surface states seem also to contribute to the deactivation process of $\operatorname{Ru}(\operatorname{bpy})_{3}^{2+*}$, though further work is necessary to prove and clarify the details of these mechanisms. Anyway, the electron transfer to the conduction band must be the main deactivation channel for $\operatorname{Ru}(\operatorname{bpy})_3^{2+}$ giving the fast decay component with less than 21-ns lifetime, for the following reasons: (i) There is a good correlation between the relative weight of the faster decay component and the energy of the conduction band edge of the substrate semiconductor relative to the redox level of $\operatorname{Ru}(\operatorname{bpy})_3^{3+}/\operatorname{Ru}(\operatorname{bpy})_3^{2+*}$. (ii) The spectrum of the fastest decay component can be assigned to $\operatorname{Ru}(\operatorname{bpy})_3^{2+}$ molecules firmly attached to the surface of semiconductors. (iii) A photosensitization effect on hydrogen evolution has been observed for the Ru- $(bpy)_3^{2+}/TiO_2$ system.

Thus, the present study confirms that $Ru(bpy)_3Cl_2$ has a considerable potential ability for sensitization of oxide semiconductors. However, close contact between the sensitizer and the semiconductor surface must be realized and the recombination of injected electrons with the oxidized sensitizer must be somehow prevented to achieve a high overall efficiency for sensitization.

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Kinetics of Gas-Phase Addition Reactions of Trichlorosilyl Radicals. 5.¹ Cis–Trans Isomerization of 2-Butene Induced by •SiCl₃ Radicals

Takaaki Dohmaru* and Yoshio Nagata

Radiation Center of Osaka Prefecture, Shinke-cho, Sakai, Osaka, 593 Japan (Received: March 1, 1982; In Final Form: August 2, 1982)

Photolytic reactions of mixtures of HSiCl₃ and cis-C₄H₈ have been investigated between 425 and 525 K in the gas phase. It was found that SiCl₃ radicals induced cis-trans isomerization of cis-C₄H₈ above 425 K. The rates of the isomerization and of the simultaneous formation of sec-C4H9SiCl3 have been measured at varying HSiCl3 concentrations. The kinetic treatment of these results leads to $\log \{k_{-1}/k_2 \pmod{\text{cm}^{-3}}\} = 3.15 \pm 0.09 - (16.7)$ \pm 0.2) kcal mol⁻¹/(2.303*RT*) where the reactions involved are \cdot SiCl₃ + *cis*-C₄H₈ \rightleftharpoons CH₃CHCH(CH₃)SiCl₃ (1, -1) and $CH_3\dot{C}HCH(CH_3)SiCl_3 + HSiCl_3 \rightarrow sec-C_4H_9SiCl_3 + \cdot SiCl_3$ (2). The value of log $\{k_{-1}/k_2 \pmod{cm^{-3}}\}$ at 475 K is -4.5 which agrees quite well with -4.4 obtained at 475 K by our previous kinetic method. From this activation energy a bond dissociation energy of $D^{\circ}(Cl_3Si-C_{sec}) = 78.3 \pm 2 \text{ kcal mol}^{-1}$ is obtained.

Introduction

In recent years there has been considerable work on gas-phase kinetics² involving silyl radicals and on the thermochemistry³ of silicon-containing compounds. But reliable quantitative information on silyl radical reactions remains very scarce compared with that for the carbon analogues.

We have studied the kinetics of .SiCl₃ radical additions to olefins^{1,4-6} for the purpose of clarifying the reaction mechanism and of obtaining the Arrhenius parameters for the elementary steps involved.

The sequence of reactions for 2-C₄H₈⁶ is

 \cdot SiCl₃ + 2-C₄H₈ \Rightarrow CH₃ĊHCH(CH₃)SiCl₃ (1)

 $CH_3\dot{C}HCH(CH_3)SiCl_3 + HSiCl_3 \rightarrow$ $sec-C_4H_9SiCl_3 + \cdot SiCl_3$ (2)

⁽¹⁾ Part 4: T. Dohmaru and Y. Nagata, Bull. Chem. Soc. Jpn., 55, 323 (1982).

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It was shown kinetically⁶ that reaction 1 was appreciably

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TABLE I: Photolysis of cis- $C_4H_s^a$ with Varying Amounts of HSiCl₃ at Various Temperatures

T/K	t ^b /min	10 ^{6.} [HSiCl ₃]/ mol cm ⁻³	$10^{2}p^{c}$	$10^2 q^d$	$10^{10} \cdot R_{sec}^{e} / (mol cm^{-3} min^{-1})$	$\frac{10^{10}}{R_{c-t}f} (mol \text{ cm}^{-3} \text{ min}^{-1})$	R_{-1}^{g}/R_{sec}	
425	30	1.37	3.26	2.1	1.89	2.98	2.62	
	30	1.92	3.16	3.1	2.85	2.90	1.69	
	30	2.74	3.04	4.0	3.62	2.80	1.29	
	30	5.48	2.65	7.4	6.74	2.48	0.609	
	190	1.37	$202 (200)^h$					
451	10	1.37	4.65	0.8	2.15	12.6	10.1	
	10	1.92	4.85	1.3	3.49	13.2	6.52	
	10	2.74	4.50	2.0	5.57	12.3	3.80	
	10	5.48	4.07	3.3	9.16	11.2	2.09	
	130	1.37	$191 (200)^h$					
477	4	1.37	3.71	0.3	2.04	25.2	21.9	
	4	1.92	4.19	0.4	2.90	28.5	17.4	
	4	2.74	4.48	0.7	4,56	30.5	11.9	
	4	5.48	4.57	1.7	11.49	31.2	4.83	
	4^i	0	0.00					
	178	1.37	$176 (0)^{h}$					
	95	1.37	$176 (180)^h$					
500	4	1.37	7.32	0.3	1.78	49.5	51.1	
	4	1.92	8.62	0.4	2.52	58.2	42.8	
	4	2.74	10.33	0.7	5.01	69.6	26.1	
	4	5.48	14.43	2.1	14.68	97.1	12.8	
	82	1.37	$171 \ (180)^h$					
525	1	1.37	3.75	0.1	1.51	102	123	
	2	1.92	9.01	0.2	2.77	122	82.9	
	2	2.74	11.52	0.3	4.56	155	65.4	
	2	5.48	18.97	1.2	16.21	253	31.7	
	30	1 37	$165(180)^{h}$					

^a $[cis-C_4H_8]_0 = 2.74 \times 10^{-7} \text{ mol cm}^{-3}$ in all runs. ^b Time of photoirradiation. ^c $p = [trans-C_4H_8]/[cis-C_4H_8]$. ^d $q = [sec-C_4H_9SiCl_3]/[cis-C_4H_8]_0$. ^e The rate of formation of $sec-C_4H_9SiCl_3$. ^f The rate of cis-trans isomerization. Calculated from eq 8. ^g Calculated from eq 12. ^h Initial composition. ⁱ In this run cis-C_4H_8 was irradiated alone.

reversible above ca. 400 K. Values of k_{-1}/k_2 were obtained for cis-C₄H₈ and trans-C₄H₈

$$\log \{k_{-1}/k_2 \text{ (mol cm}^{-3})\}_{cis} = 4.09 - 18.4 \text{ kcal mol}^{-1}/(2.303RT) (3)$$

 $\log \{k_{-1}/k_2 \text{ (mol cm}^{-3})\}_{\text{trans}} = 3.99 - 18.2 \text{ kcal mol}^{-1}/(2.303RT)$ (4)

These results can be checked most directly by investigating whether the cis-trans isomerization takes place during the sequence of reactions, since the adduct radical formed in reaction 1 can undergo rotation around the C-C bond to give a mixture of *cis*- and *trans*-butenes via reaction -1.

In the present study, we have measured the rate of isomerization and of simultaneous formation of sec-C₄H₉SiCl₃ in the photolytic reaction of cis-C₄H₈ with HSiCl₃. The value of k_{-1}/k_2 calculated in this study was compared with that from eq 3 and 4.

This is the first study giving direct evidence for the reversibility of the addition of silyl radicals to olefins. This work also extends the scope of the radical-induced cis-trans isomerization of olefins⁷ in homogeneous systems.⁸

Experimental Section

The materials were prepared, purified, and checked as described previously.⁶ Mixtures of cis-C₄H₈ and HSiCl₃ were introduced into a cylindrical quartz cell of 139 cm³ which was heated in an electrical oven. The full light from

a 50-W medium-pressure mercury arc was used. Probably very weak photoabsorption by cis-C₄H₈ in the UV region (ϵ = ca. 7 L mol⁻¹ cm⁻¹ at 2150 Å in the gas phase) initiates reactions, since HSiCl₃ was found almost transparent in this region. Once photolyzed, the reaction mixture was passed to a gas-sampling loop and was immediately analyzed by GLC; trans-C₄H₈ and cis-C₄H₈ were analyzed on a 4-m VZ-7 column (Gasukuro Kogyo Inc.), while sec-C₄H₉SiCl₃ was analyzed on a 2-m column of a mixture of SE 30 and QF-1 in a separate series of experiments.

Results and Discussion

It was found that when cis-C₄H₈ was photolyzed alone there was almost no isomerization but when cis-C₄H₈ was photolyzed with HSiCl₃, appreciable amounts of *trans*-C₄H₈ and *sec*-C₄H₉SiCl₃ but no 1-C₄H₈ were formed. The rates of formation of the products were measured between 425 and 525 K as a function of HSiCl₃ concentrations. The results are shown in Table I.

Kinetic analysis of the results is made in terms of products ratios p and R_{sec} (defined in Table I). The ratio p (= $[trans-C_4H_8]/[cis-C_4H_8]$) should, after a long time, become equal to the equilibrium constant, K, for cis-trans isomerization. For use in the subsequent kinetic analysis, one value of K was obtained at each temperature by prolonged irradiation. At 477 K, it was found from the detailed time dependence of p to require 178 min to reach equilibrium starting from pure cis- C_4H_8 . After this, however, prolonged photolyses were started from a certain value of p near the expected stationary value to keep the consumption of reactants as small as possible. The least-squares treatment of the values of K vs. 1/T in Table I gives

$K = 10^{-0.16} + 0.90 \text{ kcal mol}^{-1/(2.303RT)}$

K can also be calculated from the standard free energy

⁽⁷⁾ R. B. Cundall, "Progress in Reaction Kinetics", Vol. 2, G. Porter, Ed., Pergamon Press, 1964, Chapter 4.

⁽⁸⁾ In a heterogeneous system, however, Ono et al. studied cis-trans isomerization of $2\text{-}C_4\text{H}_8$ over siloxene and proposed a free-radical mechanism involving hydrogen-deficient silicon sites (Y. Ono, Y. Sendoda, and T. Keii, J. Am. Chem. Soc., 97, 5284 (1975)).

TABLE II: Estimated Rate Constants^a

	rate constant	value at 525 K ^b	ref
$\log k_a$	$13.5 - 3.0/\theta^{c}$	12.3	6
$\log k_a^d$		< 7.2	
$\log k_{\rm h}$	15.6 - 24.4/ heta	5.4	6
$\log k_{c}$	11.3 - 3.5/ heta	9.8	this work
$\log k_{A}$	$11.5 - 6.0/\theta$	9.0	6
$\log \mathbf{k}_{d}$		< 3.7	

^a cm³ mol⁻¹ s⁻¹ for k_a and k_d and s⁻¹ for the rest. ^b The highest temperature in this experiment. ^c $\theta = 2.303RT$ in kcal mol⁻¹. ^d k = k[HSiCl₃]. [HSiCl₃] = (1.37-5.48) × 10⁻⁶ mol cm⁻³.

change of the cis-trans isomerization: ΔG° (cis-trans) = -0.73 kcal mol⁻¹ at 298 K. This value leads to K = 3.4 which agrees quite well with K = 3.2 obtained by extrapolation of the above equation to 298 K.

As hydrogen abstraction reactions from $HSiCl_3$ are very facile reactions,^{2a} any radicals formed initially by photoabsorption of cis-C₄H₈ can produce \cdot SiCl₃ radicals via

$$\cdot R + HSiCl_3 \rightarrow RH + \cdot SiCl_3$$

The addition of \cdot SiCl₃ radicals to cis-C₄H₈ is established⁶ to proceed via free-radical chain reactions. A detailed mechanism involving addition and cis-trans isomerization is shown in eq 5. Here C and T are cis-C₄H₈ and trans-

$$\begin{array}{c} \begin{array}{c} & & \\ & \\ & \\ & \\ & \\ \end{array} \end{array} \xrightarrow{\begin{tabular}{l}{l} \\ \hline \\ & \\ & \\ \end{array} \end{array} \xrightarrow{\begin{tabular}{l}{l} \\ \hline \\ & \\ \end{array} \end{array} \xrightarrow{\begin{tabular}{l}{l} \\ \hline \\ & \\ \end{array} \xrightarrow{\begin{tabular}{l}{l} \\ \hline \\ & \\ \end{array} \end{array} \xrightarrow{\begin{tabular}{l}{l} \\ \hline \\ & \\ \end{array} \xrightarrow{\begin{tabular}{l}{l} \\ \end{array} \xrightarrow{\begin{tabular}{l}{l} \\ \hline \\ & \\ \end{array} \xrightarrow{\begin{tabular}{l}{l} \end{array} \xrightarrow{\begin{tabular}{l}{l} \end{array} \xrightarrow{\begin{tabular}{l} \end{array} \xrightarrow{\begin{tabular}{l}{l} \end{array} \xrightarrow{\begin{tabular}{l}{l} \end{array} \xrightarrow{\begin{tabular}{l} \end{array} \xrightarrow{\begin{tabular}{l}{l} \end{array} \xrightarrow{\begin{tabular}{l} \end{array} \xrightarrow{\begin{tabular}{l} \end{array} \xrightarrow{\beltibel}{l} \end{array} \xrightarrow{\beltibeltibeltibeltibeltibelti\end{array} \xrightarrow{\$$

 C_4H_8 and their adducts with $\cdot SiCl_3$ are denoted C and T, respectively.

In a previous study,⁶ we obtained k_1/k_r and k_{-1}/k_2 for $cis-C_4H_8$ and $trans-C_4H_8$ where r is a reference reaction. From these values we can estimate the approximate values of k_a , k_b , and k_d ; the value of $k_{a'}$, $k_{b'}$, or $k_{d'}$ should be nearly equal to the value of the corresponding nonprimed reaction within a factor of 2.⁶

On the other hand $k_{\rm c}$ can be calculated from the transition-state formula

$$k_{\rm c} = (\kappa T/h) K_{\rm c}^{\dagger} \exp(-E_0^{\dagger}/RT)$$

Benson et al.⁹ calculated the rate constant of the hindered internal rotation around the C–C bond of *sec*-butyl iodide radicals, CH₃CHCH(CH₃)I, by use of the above formula. Considering the structural similarity *sec*-butyl trichlorosilyl radicals, CH₃CHCH(CH₃)SiCl₃, may have a similar value, since the moment of inertia for rotation and the barrier to rotation of the ethyl radical about the C–C bond is nearly equal in both radicals. Thus we may employ the same value for k_c , namely

$$k_{\circ} = 10^{11.3 - 3.5 \text{ kcal mol}^{-1}/(2.303RT)}$$

The rate constants obtained in this way are shown in Table II. The values in Table II may not be very precise but they suggest at least $k_c >> k_b$, k_d .

The most simplified version of the mechanism (eq 5) is shown in eq 6. The steady-state treatment of eq 6 gives

$$\begin{array}{c} C & \xrightarrow{\wedge 0} \\ \star_{c-1} & \downarrow \star_{1-c} \\ T & \xrightarrow{\wedge 0^{+}} \end{array}$$
 sec - C₄H₉SiCl₃ (6)

the time dependence of p([T]/[C]) as

$$dp/dt = k_{c-t} + (k_{c-t} - k_{t-c} + k_0 - k_0)p - k_{t-c}p^2 \quad (7)$$

Integration gives

$$k_{c-t} = \frac{1}{t} \left(A^2 + \frac{4}{K} \right)^{-1/2} \ln \left(\frac{\frac{p}{A - (A^2 + 4/K)^{1/2}} - \frac{K}{2}}{\frac{p}{A + (A^2 + 4/K)^{1/2}} - \frac{K}{2}} \right)$$
(8)

where $A = 1 - 1/K + (k_0 - k_0)/k_{c-t}$ and $K = k_{c-t}/k_{t-c}$. Let the last term in A be F, then

$$F = (k_0 - k_{0'}) / k_{\rm c-t}$$

F is a measure of the correction for the consumption of $2-C_4H_8$ due to the formation of $sec-C_4H_9SiCl_3$. Assuming that F = 0 which is valid at higher temperatures (see the value of q in Table I), eq 8 is simplified to

$$k_{\rm c-t} = \frac{1}{t(1+1/K)} \ln \frac{K(p+1)}{K-p}$$
(9)

At low temperatures, however, F cannot be neglected. The steady-state treatment of eq 5 and 6 leads to eq 10; $k_c >> k_b$, \mathbf{k}_d and $k_{c'} >> k_{b'}$, $\mathbf{k}_{d'}$ were assumed (Table II).

$$k_0/k_{0'} = k_a/k_{a'} \tag{10}$$

Hence we obtain

$$F = \left(1 - \frac{k_{a'}}{k_a}\right) \left(1 + \frac{k_{a'}}{k_a}p\right)^{-1} \frac{R_{\text{sec}}}{R_{\text{c-t}}}$$
(11)

The approximate value of R_{c-t} calculated from eq 9 can be used for the purpose of evaluating F. As the value of $k_a/k_{a'}$ is already given as 1.26,⁶ we can calculate F which leads to k_{c-t} via eq 8. The values of k_{c-t} thus obtained were used to calculate R_{c-t} in Table I.

The rate of the reverse reaction (eq -1) can be expressed in terms of the rate constants in eq 5 as

$$R_{-1} = k_{\rm b}[\dot{\rm C}] + k_{\rm b'}[\dot{\rm T}]$$

This relation leads to

$$R_{-1} = \left(1 + \frac{k_{a'}}{k_a}p\right) \left(1 + \frac{k_a}{k_{a'}K}\right) R_{c-t}$$
(12)

The values of $R_{-1}/R_{\rm sec}$ were thus calculated and are also shown in Table I.

 R_{-1}/R_{sec} can be shown as a function of HSiCl_3 concentrations.

$$R_{-1}/R_{\rm sec} = (k_{-1}/k_2) [\text{HSiCl}_3]^{-1}$$
 (13)

Equation 13 requires that R_{-1}/R_{sec} be inversely dependent on the HSiCl₃ concentrations.

The data in Table I were plotted according to eq 13 in Figure 1. The plots at each temperature give a satisfactory straight line through the origin. The values of the slopes of the respective lines give the following Arrhenius equation:

 $\log \{k_{-1}/k_2 \pmod{\operatorname{cm}^{-3}}\} =$

 $3.15 \pm 0.09 - (16.7 \pm 0.2) \text{ kcal mol}^{-1}/(2.303RT)$ (14)

where the error limits are the standard deviations from the

⁽⁹⁾ S. W. Benson, K. W. Egger, and D. M. Golden, J. Am. Chem. Soc., 87, 468 (1965).



Figure 1. Plot of R_{-1}/R_{sec} vs. [HSiCl₃]⁻¹.

weighted least-mean-squares treatment.

The k_{-1}/k_2 measured based upon the rate of cis-trans isomerization (eq 14) agrees satisfactorily with those obtained by the kinetic method (eq 3 and 4).

The bond dissociation energy $D^{\circ}(\text{Si-C})$ in the adduct radical can be calculated from the value of $E_{-1} - E_2$ in eq 14. Let E_{π}° (*cis*-C₄H₈) and ΔH_1° be the π -bond energy¹⁰ of *cis*-C₄H₈ and the enthalpy of reaction 1, respectively, then

 $D^{\circ} \{ Cl_{3}Si-CH(CH_{3})\dot{C}HCH_{3} \} = E_{\pi}^{\circ}(cis-C_{4}H_{8}) - \Delta H_{1}^{\circ}$ $\Delta H_{1}^{\circ} = E_{1} - E_{-1} + \Delta nRT - \Delta C_{p}^{\circ}(T - 298)$

(10) S. W. Benson, "Thermochemical Kinetics", 2nd ed, Wiley, New York, 1976.

where ΔnRT is a conversion factor for the change in standard state and $\Delta C_p^{\circ}(T - 298)$ is the temperature correction to ΔH_1° . We have already evaluated⁶ the following values: $E_2 = 6.0$ kcal mol⁻¹, $E_1 = 3.0$ kcal mol⁻¹, $\Delta C_p^{\circ} = 4.8$ cal K⁻¹ mol⁻¹, and $E_{\pi}^{\circ}(cis\text{-}C_4\text{H}_8) = 56.8$ kcal mol⁻¹. It follows that D° {Cl₃Si-CH(CH₃)CHCH₃} = 78.3 ± 2 kcal mol⁻¹. This value agrees with the value of D° -(Cl₃Si-*i*-C₃H₇) = 80 ± 3 kcal mol⁻¹ determined by Steele et al.¹¹ using electron-impact experiments.

Potzinger et al.¹² obtained $D^{\circ}(Cl_3Si-CH_3) = 85.6$ kcal mol⁻¹ from electron-impact experiments combined with thermochemical calculations. On the other hand, Walsh and Wells¹³ obtained $D^{\circ}(Cl_3Si-CH_3) = 90.2$ kcal mol⁻¹ based upon the kinetic study of iodination of HSiCl₃. Recently Davidson^{3a} calculated enthalpies of formations of some methylsilanes by use of Benson's electrostatic model.¹⁴ The results of Davidson seem to support the method of Potzinger et al. More recently Bell et al.^{3b} calculated $D^{\circ}(Cl_3Si-CH_3) = 88.9$ kcal mol⁻¹ using the MOBI (molecular orbital bond index) method.

In order to compare our value with these values we must know the difference of $\Delta D^{\circ} = D^{\circ}(\text{Cl}_3\text{Si-CH}_3) - D^{\circ} \cdot \{\text{Cl}_3\text{Si-CH}(\text{CH}_3)\text{CHCH}_3\}$. But the experimental enthalpies of formation available for alkyltrichlorosilanes¹¹ are of questionable accuracy to obtain ΔD° .

O'Neal and Ring^{3c} recently presented the group additivity scheme for the estimation of heats of formation of alkylsilanes. There may be some problems in applying this scheme to chlorosilanes but we tentatively used it to calculate ΔD° ; the group [Si-(Cl)₃(C)] which is not tabulated in the scheme can be cancelled out in this calculation. Thus $\Delta D^{\circ} = 10.0$ kcal mol⁻¹ and then D° (Cl₃Si-CH₃) = 88.3 kcal mol⁻¹. This value lies within the range of the recent variety of values.

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$n\pi^*$ Transitions in $C_{2\nu}$ Cyclic Diones. 4-Cyclopentene-1,3-dione

Robert D. Gordon

Department of Chemistry, Queen's University, Kingston, Ontario, Canada, K7L 3N6 (Received: May 11, 1982; In Final Form: July 13, 1982)

Discrete bands in the weak visible absorption of 4-cyclopentene-1,3-dione (CPD) have been assigned to two nearly degenerate ${}^{1}B_{1} n\pi^{*} \leftarrow {}^{1}A_{1}$ transitions, involving a_{2} orbitals of mixed $\pi^{*}_{CO}/\pi^{*}_{CC}$ character, with origins at 22 008 and 22 070 cm⁻¹ (vapor) and 22 833 and 22 966 cm⁻¹ (neat crystal). Allowed and vibrationally induced components are of comparable intensity. Progressions in 332, 457, and 1451 cm⁻¹ suggest in-plane ring distortion and carbonyl bond lengthening upon excitation. A $\pi\pi^{*}$ transition is also observed near 220 nm.

Introduction

Studies of $n\pi^*$ transitions in several D_{2h} cyclic diones, including *p*-benzoquinone¹⁻⁵ and tetramethyl-1,3-cyclo-

butanedione^{6,7} and its sulfur derivatives,^{8,9} have yielded important information about the ordering of and energy

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