He I Photoelectron Spectra of Ethylene Carbonate and Related Compounds

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He I photoelectron spectra of ethylene carbonate, propylene carbonate, γ-butyrolactone, β-propiolactone and vinylene carbonate have been investigated. Assignments of an oxygen lone pair and nonbonding π orbitals have been made by means of analysis of vibrational structures and molecular orbital calculation. Many vibrational structures could be assigned to appropriate vibrational modes of the corresponding neutral molecules from a comparison with infrared and Raman spectra. Correlation among the orbital energies of the compounds is discussed.

Photoelectron spectral bands originating from the carbonyl oxygen lone pair and the nonbonding π orbitals of carbonyl compounds appear in the lower ionization energy range, lying sometimes close to each other. In the present report we deal with the photoelectron spectra of five heterocyclic carbonyl compounds, that is, ethylene carbonate and related compounds. The related compounds are derived from ethylene carbonate by the following substitution: 1) replacement of a hydrogen atom by a methyl group, 2) replacement of an esteric oxygen by a methylene group, 3) removal of an esteric oxygen, and 4) change of the single bond between the ethylenic carbons into a double bond. Their constitutional formulas are shown in Fig. 1.

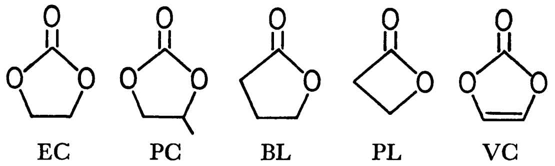

Fig. 1. Structural formulas of compounds investigated. EC: Ethylene carbonate, PC: propylene carbonate, BL: γ-butyrolactone, PL: β-propiolactone, VC: vinylene carbonate.

It has been proved that a comparison of a series of related compounds is useful for the assignment of their spectral bands to a particular molecular orbital, and that analysis of vibrational structures in some bands can be utilized for band assignment. By these means the effects of substitution on orbital energy and also orbital character could be clarified.

Experimental

He I resonance line at 58.4 nm emitted from a direct current discharge tube was used as an excitation light source. The discharge tube was so designed as to intensify the resonance line and to obtain photoelectron spectra of high signal-to-noise ratio. It has two coaxially aligned hollow electrodes and collimator capillaries to introduce the light produced within the whole discharge area into the ionization chamber. The photoelectron energy analyzer used was of a parallel plate type.[1] Xe gas was mixed with sample gas and used as an internal standard. A half width of Xe $2p_{3/2}$ peak was approximately 30 meV. The organic compounds used showed a tendency to broaden Xe peaks, probably due to in homogeneity of the surface potential caused by the adsorption of sample gas onto the analyzer electrodes.

Variation in room temperature caused a drift of the position of peaks, probably due to the variation in adsorption equilibrium caused by a change of the sample pressure. The ionization energy was therefore determined by measuring the sample peak and internal standard peak alternately several times. Coating of the electrode surface with graphite emulsion effectively lowered the background of the spectrum. Better resolution was obtained at a sample pressure above the pressure range in which there is a linear relation between sample pressure and spectral intensity. This might be related to the neutralization of the space charge in the ionization chamber by backscattered electrons and to the saturation of adsorbed sample gas.

Vinylene carbonate was synthesized from chloroethylene carbonate,[2,3] and purified by vacuum distillation. All the other compounds were chemicals of G. R. grade and used without purification. Samples in which residual water was detected were used after dehydration with anhydrous sodium sulfate or phosphorus pentoxide.

Laser Raman spectra of the three carbonates were taken for reference in the vibrational analysis of their photoelectron spectra.

Results and Discussion

Ethylene Carbonate and Propylene Carbonate. The lowest energy overlapping bands in the photoelectron spectra

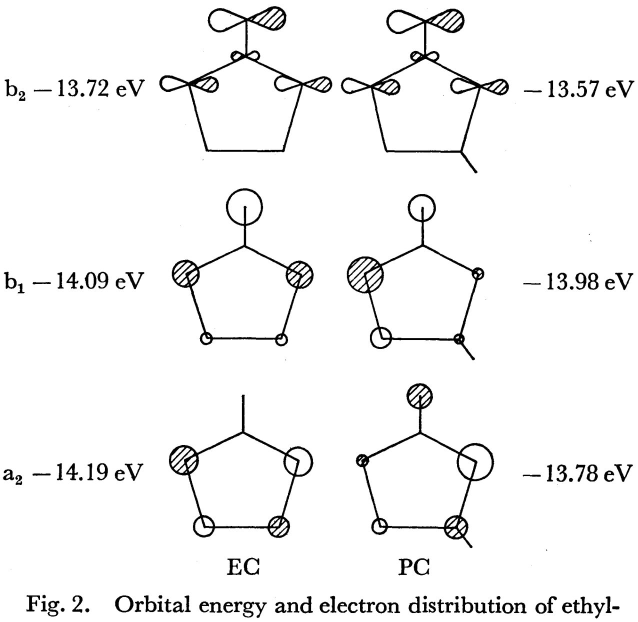

Fig. 2. Orbital energy and electron distribution of ethylene carbonate(EC) and propylene carbonate(PC) obtained from INDO calculation.

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TABLE 1. IONIZATION ENERGY AND VIBRATIONAL FREQUENCY OF ETHYLENE CARBONATE AND PROPYLENE CARBONATE

	Band	Ionization energy, eV		Vibrational frequency, cm^{-1}		Band assignment
		adiabatic	vertical	ion	molecule	
Ethylene carbonate	1 st	10.70	10.89	1530 910	1765—1790$^{a)}$ 1065$^{b)}$	$n_O(5b_2)$
	2 nd		11.38			$\pi(2a_2)$
	3 rd		11.45			$\pi(3b_1)$
Propylene carbonate	1 st	10.52	10.71	1520 820	1785$^{a)}$ 960$^{b)}$	$n_O(b_2)^{c)}$
	2 nd		11.17			$\pi(a_2)^{c)}$
	3 rd		11.27			$\pi(b_1)^{c)}$

a) Carbonyl stretching vibration. b) Skeletal stretching vibration. c) Propylene carbonate does not belong to the point group C_{2v}. However, the respective orbitals can be associated with b_2, a_2, and b_1 orbitals of ethylene carbonate from electron distribution.

of ethylene carbonate and propylene carbonate have been assigned to three appropriate molecular orbitals as a result of analysis of vibrational structures and INDO molecular orbital calculation.[4] The ionization energies and vibrational frequencies are given in Table 1. Figure 2 shows the orbital energies and electron distributions of ethylene carbonate and propylene carbonate obtained from the molecular orbital calculation.

Several reports have appeared on the ionization energies of the carbonyl oxygen lone pair orbital of ethylene carbonate.[5–8] However, there are discrepancies among the reported values both for the adiabatic and vertical ionization energies. We pointed out that the vertical ionization energy corresponds not to the highest peak but to the second peak in the main vibrational progression, this conclusion being derived from the reasoning that the second peak should be the most intense if the relative intensity of the peaks in the vibrational progression is not modified by the slope of the adjacent bands.[4]

The adiabatic ionization energy and the frequency of carbonyl stretching vibration we determined are consistent with the results obtained by Sweigart and Turner[5] (10.70 eV and 1500 cm^{-1}), but not with those by McGlynn *et al.*[7,8] (10.40 eV and approx. 1900 cm^{-1}). Variation in room temperature during the course of measurement causes a change of sample pressure in the sample reservoir, leading to apparent drift of ionization energy. Since the lowest energy overlapping bands obtained by McGlynn *et al.* are identical with ours and they used the same energy reference (Xe $2p_{3/2}$ 12.130 eV) as we did, the only possible explanation for the discrepancies seems to be a drift in the ionization energy in their measurement. Contraction of the ionization energy scale with the Xe $2p_{3/2}$ peak as a base point would result in a lowering of the adiabatic ionization energy and at the same time an increase in the vibrational frequency. The direction of the shift of their values relative to ours is in line with the above inference. Contrary to their results, the frequency of the carbonyl stretching vibration of the neutral molecule is usually reduced on ionization from the carbonyl oxygen lone pair orbital.

The vibrational spacing of the subsidiary vibrational progression in the first band is 910 and 820 cm^{-1} for ethylene carbonate and propylene carbonate, respectively.[4] The vibration should correspond to one of the skeletal stretching modes. Two skeletal stretching vibrations appear in the Raman spectra of ethylene carbonate (980 and 1065 cm^{-1}) and propylene carbonate (1125—1150 and 960 cm^{-1}). In many cases the ionization from a molecular orbital with almost the same electron distribution gives nearly the same reduction ratio of vibrational frequency of a neutral molecule to the corresponding cation among different molecules. Thus the vibrational frequencies giving the common reduction ratio, which is calculated to be 0.85, are 1065 cm^{-1} (for ethylene carbonate) and 960 cm^{-1} (for propylene carbonate). Angell[9] denoted the skeletal stretching vibrations of 980 and 1065 cm^{-1} in infrared spectra of ethylene carbonate by ν_4 and ν_5, respectively, which belong to the irreducible representation A_1. Thus the analysis of photoelectron spectra shows that the skeletal stretching vibration of 960 and 1125—1150 cm^{-1} in the Raman spectrum of propylene carbonate should

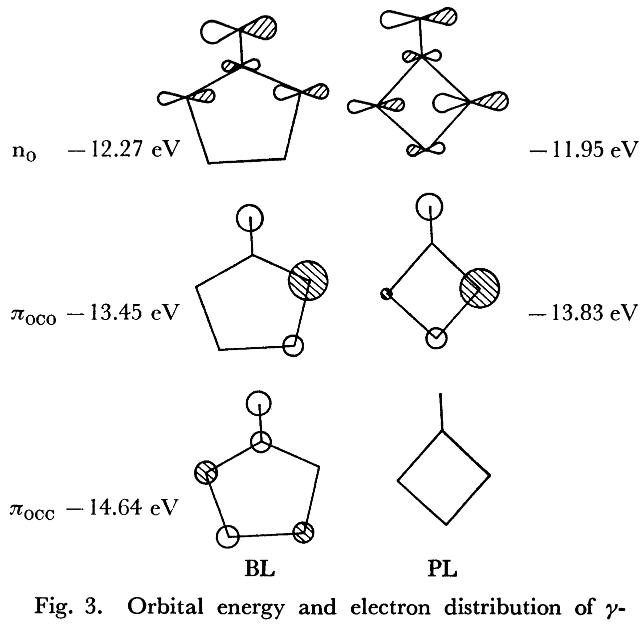

Fig. 3. Orbital energy and electron distribution of γ-butyrolactone(BL) and β-propiolactone(PL) obtained from INDO calculation. The esteric oxygen occupies the same position as shown in Fig. 1.

correspond to ν_5 and ν_4 in ethylene carbonate, respectively, *viz.*, a reversal in magnitude of the vibrational frequency of the two vibrational modes. This result shows that the methyl substituent effect on the frequency of skeletal stretching modes differs for ν_4 and ν_5. This effect could not be revealed by analysis of Raman or infrared spectra alone, even when the spectra for both carbonates were compared with each other.

γ-Butyrolactone and β-Propiolactone. Characteristic bands related to the ionization from the carbonyl oxygen lone pair and the nonbonding π orbitals were also studied for γ-butyrolactone and β-propiolactone in relation to ethylene carbonate. INDO molecular orbital calculation was made for these two lactones on the assumption of planar molecular configuration. The results are given in Fig. 3. The calculation shows that there are considerable differences between these compounds. Firstly, the lone pair orbital of γ-butyrolactone, $n_{O\gamma}$, is localized mainly on the two oxygen and one carbon atoms. On the other hand, that of β-propiolactone, $n_{O\beta}$, is fairly delocalized over all the skeletal atoms so that the electron density on the esteric oxygen atom is almost equal to that on the carbonyl oxygen atom. Secondly, γ-butyrolactone contains two π orbitals which can be thought to have a nonbonding character from the similarity in nodal plane to the nonbonding π orbitals of ethylene carbonate. They will be denoted by π_{OCO} and π_{OCC} according to the electron distribution. On the other hand, only one of the nonbonding π orbitals remains in β-propiolactone, which will be denoted by π'_{OCO}, corresponding to the orbital π_{OCO} in γ-butyrolactone.

The whole photoelectron spectra of γ-butyrolactone and β-propiolactone are shown in Fig. 4. The first band of γ-butyrolactone has several vibrational fine structures, as shown in Fig. 5. There are four main peaks with vibrational spacings of approximately 1530 cm^{-1}, which could be attributed to the excitation of the carbonyl stretching mode of the ion. The first band could be assigned to ionization from the carbonyl oxygen lone pair orbital, $n_{O\gamma}$. These spacings are almost equal to those of the n_O bands of ethylene carbonate and propylene carbonate. The three compounds give four sharp or prominent main peaks in the first band corresponding to the ionization from the lone pair orbitals. The number of fine structures shows that the change of geometry from neutral molecule to ion or the Franck-Condon factor seems to be almost equal to each other. It would be said that the degrees of localization of the lone pair orbital are almost equal among these molecules. There are further three weak peaks on the higher ionization energy side of each main peak of γ-butyrolactone, which are not seen in the spectrum of ethylene carbonate. Vibrational spacings from each main peak are approximately 340, 830, and 1130 cm^{-1} for the three peaks. From a comparison with the infrared and Raman spectra, the vibrational spacings of 1130 cm^{-1} might be attributed to the excitation of the skeletal stretching mode of the ion, which is 1170 cm^{-1} in the neutral molecule. Appearance of two more vibrational excitations for γ-butyrolactone should be attributed to the substitution of a methylene group for an oxygen atom in ethylene carbonate and, at the same time, change of molecular symmetry. The adiabatic and vertical ionization energies of the first band of γ-butyrolactone are 10.06 and 10.26 eV, respectively. The vertical one is identical to the value reported by Bain and Frost.6)

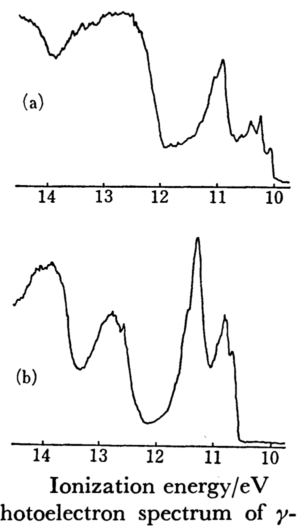

Fig. 4. (a) Photoelectron spectrum of γ-butyrolactone. (b) Photoelectron spectrum of β-propiolactone.

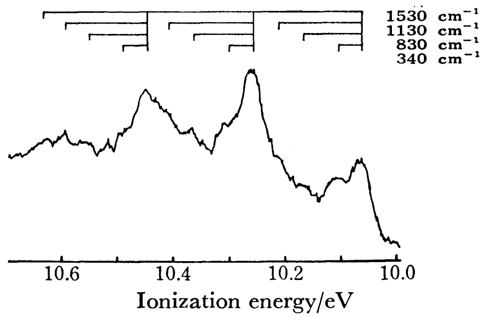

Fig. 5. First band of photoelectron spectrum of γ-butyrolactone.

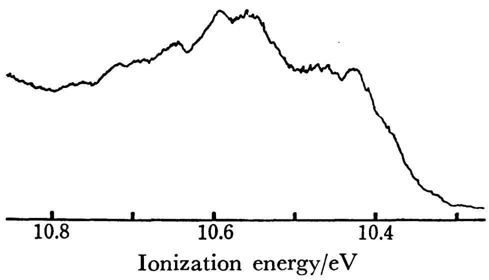

Fig. 6. First band of photoelectron spectrum of β-propiolactone.

The orbitals of the first band in the photoelectron spectrum of β-propiolactone are shown in Fig. 6. There are many peaks, but they are very complex and cannot be attributed to any harmonic vibrational progressions. This tendency has been reported as regards the photoelectron spectra of cycloalkanones.10) Cyclobutanone gives a complex first band, while cyclopentanone clearly shows some vibrational progressions. The complexity may be due to the change in hybridization of the lone pair orbital of the carbonyl oxygen atom resulting from the strain of the ring. In fact, the results of molecular orbital calculations shown in Fig. 3 indicate a marked change in electron distribution, *viz.*, the delocalization of $n_{O\beta}$ orbital over all the skeletal atoms. The somewhat unusual aspect of the first band of β-propiolactone seems to be associated with the result of infrared study by Durig,[11] which showed that the vibration of this molecule is very anharmonic.

The second band of γ-butyrolactone can be compared with the second band of β-propiolactone. Each second band has a shoulder on its higher ionization energy side. These peaks are fairly broad as compared with those in the first band. The second bands in the two spectra can be assigned to the ionization from the approximately nonbonding π orbital, π_{OCO} in γ-butyrolactone and π'_{OCO} in β-propiolactone from the results of molecular orbital calculation and the similarity in spectral shapes. Intensity ratios of the π band to the first band are almost equal for the two compounds, indicating that only one orbital is involved in the second band of γ-butyrolactone. The spacing between the shoulder and the main peak could not be attributed to any vibrational progression, since the peak for the adiabatic ionization cannot be distinguished. The vertical ionization energy of π_{OCO} orbital for γ-butyrolactone is 10.93 eV and that of π'_{OCO} orbital for β-propiolactone is 11.20 eV.

The molecular orbital calculation predicts that the second nonbonding π orbital, π_{OCC}, of γ-butyrolactone should exist approximately 1 eV below the first nonbonding π orbital, and that three σ orbitals cluster together with the second nonbonding π orbital in an energy range of approximately 2 eV. As a matter of fact, the photoelectron spectrum of γ-butyrolactone indicates that the third band begins to rise at 12 eV (approximately 1 eV higher than the second band), and that a number of bands overlap in the energy range 12—14 eV, supporting the prediction of the molecular orbital calculation. Thus the adiabatic ionization energy of the π_{OCC} orbital could be estimated to be 12 eV or higher. The results are summarized in Table 2.

Vinylene Carbonate. Vinylene carbonate is a cyclic carbonate ester of the hypothetical enediol and differs from ethylene carbonate in having a double bond in the ring structure. The molecule is considered to have a planar configuration and consequently C_{2v} symmetry in gaseous phase from the results of microwave spectroscopic study by Slayton *et al.*[12] Infrared and Raman spectroscopic studies for this molecule were carried out by Dorris *et al.*[13]

The photoelectron spectrum of vinylene carbonate gives three well separated prominent bands in the lower ionization energy region. Each of the three bands shows distinct vibrational progressions.

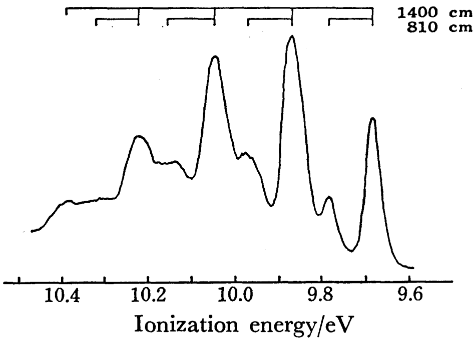

Fig. 7. First band of photoelectron spectrum of vinylene carbonate.

The first band (Fig. 7) has five main peaks with vibrational spacings of approximately 1400 cm^{-1}, each main peak being accompanied by one subsidiary peak. The spacings between the subsidiary and main peaks are approximately 810 cm^{-1}.

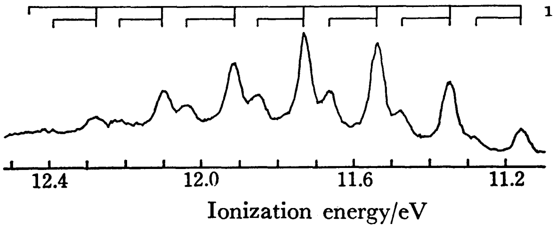

Fig. 8. Second band of photoelectron spectrum of vinylene carbonate.

The second band (Fig. 8) has at least eight main peaks with vibrational spacings of approximately 1510 cm^{-1} and subsidiary peaks approximately 990 cm^{-1} apart from each main peak.

The third band (Fig. 9) is on the slope of the next broad band, having at least four main peaks with vibrational spacings of approximately 1900 cm^{-1}. Each main peak is accompanied by three subsidiary peaks,

TABLE 2. IONIZATION ENERGY AND VIBRATIONAL FREQUENCY OF γ-BUTYROLACTONE AND β-PROPIOLACTONE

	Band	Ionization energy, eV		Vibrational frequency, cm^{-1}		Band assignment
		adiabatic	vertical	ion	molecule	
γ-Butyrolactone	1 st	10.06	10.26	1530		n_O
				1130	1170[a]	
				830		
				340		
	2 nd		10.93			π_{OCO}
	3 rd	>12.0				π_{OCC}
β-Propiolactone	1 st		10.7	anharmonic		n_O
	2 nd		11.20			π_{OCO}

a) Skeletal stretching vibration.

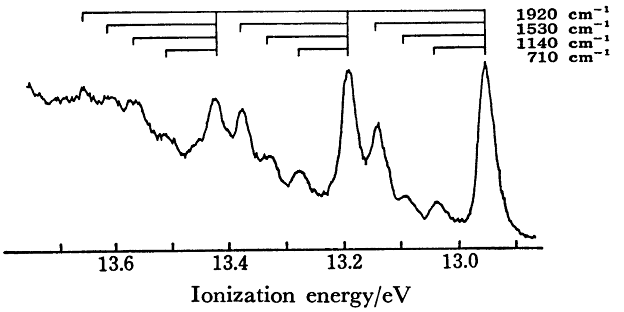

Fig. 9. Third band of photoelectron spectrum of vinylene carbonate.

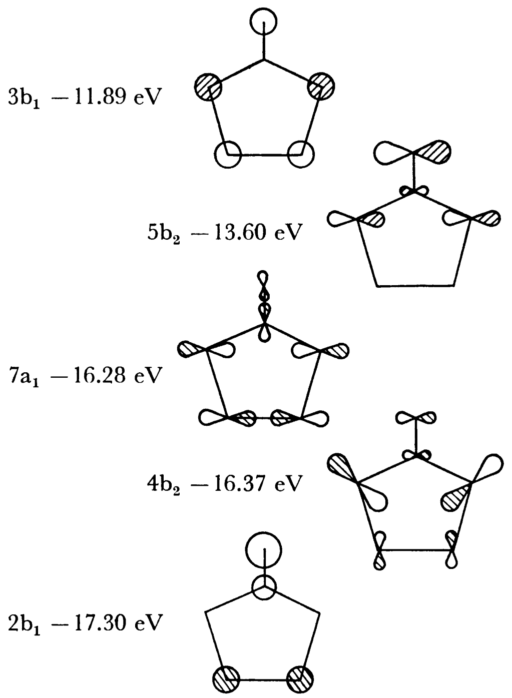

Fig. 10. Orbital energy and electron distribution of vinylene carbonate obtained from INDO calculation.

approximately 1530, 1140, and 710 cm^{-1} apart from each main peak.

INDO molecular orbital calculation shows possible orbitals to be assigned to these three bands (Fig. 10), which are denoted by $3b_1$, $5b_2$, $7a_1$, $4b_2$, and $2b_1$ after the notations for ethylene carbonate. The double bond in the ring structure changes the situations of some orbitals.

The $5b_2$ and $4b_2$ orbitals of vinylene carbonate are almost equal in energy to the $5b_2$ and $4b_2$ orbitals, respectively, of ethylene carbonate. However, introduction of the double bond into the ring structure results in the promotion of the $3b_1$ orbital energy above the $5b_2$ orbital energy. The results of calculation indicate that the $3b_1$ orbital should have the lowest ionization energy. This was confirmed by the following vibrational analysis of the photoelectron spectrum of vinylene carbonate. The vibrational spacings of approximately 1400 cm^{-1} in the first band would correspond to the excitation of the skeletal stretching mode reduced from 1625 cm^{-1} in the neutral molecule. The vibrational mode is mainly dominated by the vibration between the ethylenic carbons. Thus such a reduction suggests the ionization from an orbital having a bonding character between the ethylenic carbons, such as $3b_1$, $7a_1$, and $2b_1$ orbitals. Since the orbital energy of $3b_1$ orbital is raised higher than that of the highest occupied π orbital of ethylene (-10.5 eV) by introduction of vinylene group, the first band could be assigned to $3b_1$ orbital (*cf.* Section "Correlation of Orbital Energies of Five Compounds). The vibrational spacings of approximately 810 cm^{-1} could be ascribed to the skeletal breathing vibration in the ion reduced from 911 cm^{-1} in the neutral molecule. The adiabatic and vertical ionization energies can easily be determined to be 9.68 and 9.87 eV, respectively.

The results of calculation also predict that the second band corresponds to the ionization from the $5b_2$ orbital. The vibrational spacings of approximately 1510 cm^{-1} in the main vibrational progression would correspond to the carbonyl stretching mode in relation to the assignment in the previous sections. Thus the second can be assigned to the ionization from the $n_O(5b_2)$ orbital in accordance with expectation from the calculated orbital energy. The spacings of approximately 990 cm^{-1} would correspond to the skeletal stretching mode reduced from 1100 cm^{-1} in the neutral molecule. The skeletal stretching frequency of the ions is higher than that of ethylene carbonate. The reduction ratio of the frequency is approximately 0.90, indicating that the change in skeletal bonding strength is somewhat smaller than that of ethylene carbonate. The discrepancy would be caused by the existence of the double bond in the ring structure of vinylene carbonate. At least eight components appear in the main vibrational progression ascribed to carbonyl stretching, while there are only four components in the lone pair photoelectron band of ethylene carbonate. This implies that the molecular geometry is rather largely changed by the ionization from the $5b_2$ orbital than in ethylene carbonate. The change in carbonyl oxygen-carbon distance seems similar to that of ethylene carbonate where the reduction ratio is approximately 0.82. Many vibrational components are found in the band corresponding to the ionization accompanied by a drastic change of molecular symmetry, *e.g.* in the first band of ammonia (pyramidal to planar). It could thus be said that not only the carbonyl carbon-oxygen distance but also the C_{2v} symmetry in the neutral molecule change with the photoionization from the $5b_2$ molecular orbital of vinylene carbonate. The adiabatic and vertical ionization energies for the $5b_2$ lone pair orbital of vinylene carbonate are 11.16 and 11.73 eV, respectively. The vertical one differs from the value reported by Bain and Frost[6] by a unit of vibrational spacings, approximately 0.19 eV.

The vibrational spacings of approximately 1900 cm^{-1} in the third band are considerably large compared with the largest possible vibration of the neutral molecule. In this case, it is necessary to refer to the characters of molecular orbitals. From the results of calculation, any of the $7a_1$, $4b_2$, and $2b_1$ orbitals around -16.5 eV could be taken for the third band. Their orbital energies seem to be almost degenerate from molecular orbital calculation alone and it would be impossible to choose an appropriate one among them. In this case the characteristic vibrational spacings mentioned above could be used as a clue to the assignment of the third band. A possible mode of vibration to be assigned to the vibrational spacings of approximately 1900 cm^{-1} is the carbonyl stretching or the skeletal stretching involving the carbon-carbon double bond stretching. The $7a_1$ molecular orbital has a strong bonding character between the double bond in the ring structure. It has also the same character for the carbon-oxygen double bond of the carbonyl group. If an electron is ionized from this orbital, these bonds would reduce their bonding character. As a result, the vibrational frequencies corresponding to these bonds should be reduced relative to those in the neutral molecule. This orbital is not suitable for explaining the high frequency in the ion. The same discussion can also be applied to the case of the $2b_1$ orbital. The $4b_2$ orbital reveals a bonding character in the carbon-oxygen double bond and an antibonding character in the carbon-carbon double bond. The ionization of an electron from such an orbital would cause a desirable change, *viz.*, carbon-carbon double bond in the ring should be stronger in the ion than in the neutral molecule. The vibrational spacings of approximately 1900 cm^{-1} could be attributed to the skeletal stretching mode of the ion, the wave number of which is 1625 cm^{-1} in the neutral molecule. Thus, the third band could be assigned to the ionization from the $4b_2$ orbital. Necessarily the vibrational spacings of approximately 1530 cm^{-1} could be attributed to the carbonyl stretching mode reduced from 1830 cm^{-1} in the molecule and the spacings of 1140 and 710 cm^{-1} could be attributed to the skeletal breathing and skeletal stretching mode which are 911 and 1100 cm^{-1}, respectively, in the neutral molecule. A study by means of group theory shows that five vibrational modes belonging to an irreducible representation A_1 are possible for six atoms except C–H vibrations. Four of them can be found in the third band showing that the $4b_2$ orbital is actually distributed on the whole skeletal structure. The other one is the carbonyl bending vibration which would not be excited through a photoionization process. The results are summarized in Table 3.

Correlation of Orbital Energies of Five Compounds. The vertical ionization energies of the oxygen lone pair and nonbonding π orbitals of the five compounds are shown in the form of a correlation diagram in Fig. 11. Propylene carbonate, γ-butyrolactone, and β-propiolactone do not belong to the point group C_{2v}. However, the π orbitals of these compounds can be associated with the b_1 or a_2 orbital of ethylene carbonate from a consideration of electron distribution.4)

TABLE 3. IONIZATION ENERGY AND VIBRATIONAL FREQUENCY OF VINYLENE CARBONATE

Band	Ionization energy, eV		Vibrational frequency, cm^{-1}		Band assignment
	adiabatic	vertical	ion	molecule	
1 st	9.68	9.87	1400	1625b)	$\pi(3b_1)$
			810	911c)	
2 nd	11.16	11.73	1510	1830a)	$n_O(5b_2)$
			990	1100b)	
3 rd	12.95	12.95	1900	1625b)	$(4b_2)$
			1530	1830a)	
			1140	911c)	
			710	1100b)	

a) Carbonyl stretching vibration. b) Skeletal stretching vibration. c) Skeletal breathing vibration.

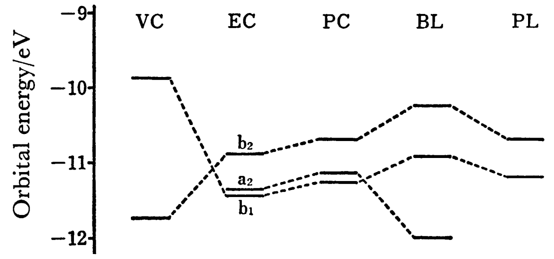

Fig. 11. Correlation diagram of observed orbital energies for ethylene carbonate and related compounds.

Oxygen Lone Pair Orbital n_O: The orbital of propylene carbonate is destabilized (0.18 eV) relative to ethylene carbonate due to the electron releasing effect of methyl group.4) The orbital of γ-butyrolactone is destabilized (0.63 eV) as a result of the substitution of esteric oxygen with methylene, which is less electronegative than the former. The degree of orbital stabilization of β-propiolactone relative to γ-butyrolactone (0.44 eV) is approximately the same as that of cyclobutanone relative to cyclopentanone (0.36 eV), which was attributed to the hybridization change as well as an inductive effect of a methylene chain.10) The orbital stabilization of vinylene carbonate relative to ethylene carbonate (0.84 eV) is in line with that of cyclopenten-3-one relative to cyclopentanone (approximately 0.2 eV), which could also be attributed to the greater electronegativity of sp^2-carbons as compared with sp^3-carbons.14,15)

Nonbonding π *Orbitals*: The nonbonding π orbitals of propylene carbonate destabilize (approximately 0.2 eV) relative to the corresponding orbitals of ethylene carbonate due to the electron releasing effect of methyl group. γ-Butyrolactone and β-propiolactone belong to the point group C_s in a planar molecular configuration. When the molecular symmetry is lowered from C_{2v} to C_s, the representations B_1 and A_2 are changed to A'', and the b_1 and a_2 orbitals go over into a'' orbitals. Thus the accidentally degenerate b_1 and a_2 orbitals of ethylene carbonate can interact with each other to generate the π_{OCO} and π_{OCC} orbitals in γ-butyrolactone. Inspection into the electron distribution shows that the π_{OCO} orbital is more closely related to the b_1 orbital and the π_{OCC} orbital to the a_2 orbital. Destabilization of the π_{OCO} orbital (0.52 eV) could result from both the substitution of an esteric oxygen with methylene and the interaction, accompanied by the stabilization of the π_{OCC} orbital ($<$0.6 eV). π_{OCC} orbital stabilization of β-propiolactone relative to γ-butyrolactone (0.27 eV) could be explained by an inductive effect of a methylene chain.

In contrast to the n_O orbital the nonbonding $\pi(b_1)$ orbital of vinylene carbonate is destabilized (1.58 eV) relative to the corresponding orbital of ethylene carbonate. The destabilization could be explained by assuming that the two carbonates are a composite molecule of a localized carbonate and a localized hydrocarbon groups (ethylene and vinylene groups, respectively) and that symmetric π orbitals of the carbonate and hydrocarbon groups combine in a reversed phase to produce the $\pi(b_1)$ orbital. The energy of the symmetric π orbitals of the vinylene group was taken as -10.51 eV from the energy of the highest occupied π orbital of ethylene.16) That of the ethylene group (-15.4 eV) was adopted from the energy of ethane $1e_u$ orbital which belongs to the pseudo-π molecular orbitals built from e-type methyl orbitals.17) The energy of the symmetric π orbital of the carbonate group cannot readily be estimated. However, it should be around -12 or -13 eV, since the energy level of an oxygen π orbital is found around this energy range in such molecules as water, formic acid *etc*. Thus, the symmetric π orbital of the vinylene group lies higher than the corresponding one of the carbonate group. In ethylene carbonate the b_1 orbital is somewhat destabilized relative to the orbital energy of the carbonate group due to the interaction between the orbitals of the ethylene and the carbonate groups. In vinylene carbonate, on the other hand, such an interaction leads to the destabilization of the b_1 orbital higher up than the orbital energy of the vinylene group.

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