

Short Communications

Molecular Vibrations and Mean Amplitudes of Carboxylic Acids

III. Oxalic Acid Monomer

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Recently Náhlovská *et al.*¹ have investigated gaseous oxalic acid in infrared and electron diffraction. They quote some results of mean amplitudes (u) and perpendicular amplitude correction coefficients (K) from a preliminary analysis in this laboratory; cf. columns c_4 and c_5 in Table 2 of Ref. 1. Furthermore, they report an unsuccessful attempt of applying the spectroscopical K values in an analysis of the average structure of the molecule.

In the present note we wish to communicate the final results of computed u and K values, because most of them deviate substantially from the preliminary ones.¹ The electron diffraction data¹ were used as equilibrium structure parameters. An initial approximate force field was obtained by means of transferable force constants from formic² and acetic³ acid monomers. Unfortunately a complete assignment of vibrational frequencies for oxalic acid is not available. In the present work observed data from different sources^{1,4,5} were used along with calculated frequencies in a tentative assignment as shown in Table 1. The established final force constants, which were adjusted to fit exactly the given assignment, were used to calculate the mean amplitudes (u) and perpendicular amplitude correction coefficients (K) with the results reported in Tables 2 and 3, respectively.

The calculated u values show about as good agreement with the electron diffraction results¹ as could be expected. The largest discrepancies occur in the case

Table 1. Tentative assignment of observed and calculated frequencies for oxalic acid monomer.

Species	No.	$\omega(\text{cm}^{-1})$	Approximate mode
A_g	1	3506	$\nu(\text{O}-\text{H})$
	2	2237	$\nu(\text{C}=\text{O})$
	3	1762 ^a	$\nu(\text{C}-\text{C})$
	4	1457 ^a	$\delta(\text{C}-\text{O}-\text{H})$
	5	852 ^a	$\delta(\text{C}-\text{C}=\text{O})$
	6	590 ^a	$\nu(\text{C}-\text{O})$
	7	432 ^a	$\delta(\text{C}-\text{C}-\text{O})$
B_g	1	869	
	2	505	
A_u	1	696	
	2	471	
	3	90	
B_u	1	3475 ^b	$\nu(\text{O}-\text{H})$
	2	1820 ^c	$\nu(\text{C}=\text{O})$
	3	1325 ^c	$\delta(\text{C}-\text{O}-\text{H})$
	4	1240 ^c	$\nu(\text{C}-\text{C})$
	5	656	$\delta(\text{C}-\text{C}=\text{O})$
	6	480	$\delta(\text{C}-\text{C}-\text{O})$

^a Ref. 4. ^b Ref. 1. ^c Ref. 5.

of the three long $\text{O}\cdots\text{O}$ distances and $\text{C}\cdots\text{O}_2'$, for which all the calculated values appear to be too low (cf. Table 2). Considerably higher values were obtained from the preliminary spectroscopical analysis,¹ which indicates that the values are sensitive for different choices of vibrational assignments. For glyoxal at 298°K the calculated values of u corresponding to $\text{C}\cdots\text{O}_2'$ and $\text{O}_2'\cdots\text{O}_2'$ are ⁶ 0.062 Å and 0.060 Å, respectively. These results suggest that the u values calculated here for the corresponding distances really may be about 0.005 to 0.010 Å too low, but they

Table 2. Mean amplitudes of vibration (u) for oxalic acid.

Distance ^a	(Equil.) ^b	u in Å			E.D. ^c u (σ) ~160°C
		$T=0$	298.16	433.16°K	
H—O ₁	(1.056)	0.071	0.071	0.071	
C—O ₁	(1.339)	0.043	0.044	0.045	0.0448 (0.0022)
C=O ₂	(1.208)	0.037	0.037	0.038	0.0361 (0.0020)
C—C'	(1.548)	0.043	0.044	0.045	0.0526 (0.0048)
C...O ₁ '	(2.395)	0.053	0.055	0.059	0.0681 (0.0080)
C...O ₂ '	(2.429)	0.050	0.052	0.055	0.0742 (0.0100)
O ₁ ...O ₂	(2.260)	0.052	0.054	0.058	0.0597 (0.0030)
C...H	(1.900)	0.097	0.098	0.099	
C...H'	(2.218)	0.124	0.127	0.132	
O ₁ ...O ₁ '	(3.558)	0.057	0.061	0.067	0.1183 (0.0193)
O ₂ ...O ₂ '	(3.510)	0.052	0.055	0.059	0.0763 (0.0064)
O ₁ ...O ₂ '	(2.717)	0.064	0.072	0.080	0.1139 (0.0042)
H...O ₂	(3.052)	0.095	0.095	0.097	
H...O ₂ '	(2.044)	0.128	0.135	0.144	
H...O ₁ '	(3.542)	0.128	0.131	0.137	
H...H'	(3.829)	0.157	0.160	0.165	

^a Identification of atoms as in Ref. 1.

^b Calculated interatomic separations (in Å) from the applied structural parameters.

^c From Ref. 1.

should not be as high as the results of the preliminary analysis.¹ Otherwise the corre-

Table 3. Perpendicular amplitude correction coefficients (K) for oxalic acid.

Distance ^a	K in Å		
	$T=0$	298.16	433.16°K
H—O ₁	0.020	0.024	0.028
C—O ₁	0.004	0.010	0.014
C=O ₂	0.003	0.005	0.007
C—C'	0.002	0.002	0.002
C...O ₁ '	0.002	0.006	0.008
C...O ₂ '	0.001	0.002	0.003
O ₁ ...O ₂	0.003	0.012	0.016
C...H	0.014	0.026	0.034
C...H'	0.010	0.020	0.026
O ₁ ...O ₁ '	0.000 ₃	0.000 ₄	0.000 ₅
O ₂ ...O ₂ '	0.000 ₄	0.000 ₅	0.000 ₆
O ₁ ...O ₂ '	0.002	0.009	0.013
H...O ₂	0.009	0.021	0.028
H...O ₂ '	0.013	0.031	0.042
H...O ₁ '	0.005	0.006	0.007
H...H'	0.009	0.010	0.012

^a See footnote to Table 2.

spondence between the values of u calculated here and those of corresponding distances in glyoxal² and formic acid³ is perfect.

The calculated K values (Table 3) should not be accepted without precaution, especially because of the lack of observed out-of-plane vibrational frequencies. But the set is believed to be an improvement of the preliminary data.¹

It was also attempted to refine the present calculations by including a potential parameter for the hydrogen bond, as was successfully applied to formic acid monomer.³ Following the same procedure it was found that the imposing of $h=0.5$ mdyne/Å and subsequent adjustment to the assigned frequencies made the u value for the hydrogen bond drop from 0.14 Å to 0.12 Å at 433°K. Simultaneously the u values for the following distances were lowered by about 0.01 Å: C...H', H...O₁', and H...H'. None of the u values for these distances are observed in the electron diffraction experiment; hence it is difficult to draw any certain conclusion about the significance of a potential parameter for the hydrogen bond in the present case.

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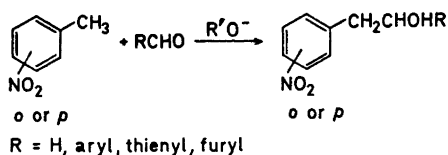
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The Photocyclization of 2-(*o*-Nitrophenyl)-ethanol to *N*-Hydroxyoxindole

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A facile method for the addition of *o*- and *p*-mononitrotoluenes to aldehydes has been reported.¹ By that method, 2-(nitro-aryl)-ethanols became available free from the isomers.

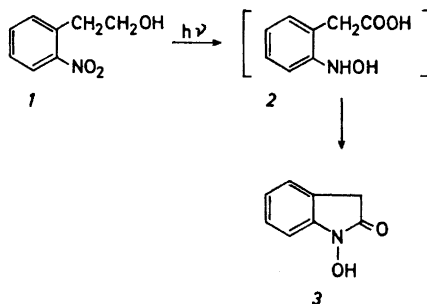


We have studied the chemistry of some of these ethanols.² The present communication will deal with a photochemical reaction of 2-(*o*-nitrophenyl)-ethanol (*1*). The irradiation of 2-(*o*-nitrophenyl)-ethanol in ethanol gave an acidic, crystalline product. IR spectroscopy showed the compound

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to contain a carbonyl group (1685 cm^{-1}), a strongly hydrogen bonded hydrogen atom (broad band from 3200 to 2500 cm^{-1}) and no nitro group.

The oxidising power of the photo-excited nitro group is well known.^{3,4} Oxidation of the hydroxyl group in compound *1* by the nitro group would hypothetically give 2-(*o*-hydroxylaminophenyl)-acetic acid (*2*) which could cyclize to *N*-hydroxyoxindole (*3*):



The product, purified by chromatography and recrystallisation, had IR, m.p., and mixed m.p. (both 199 – 200°) identical to those of an authentic sample⁵ of *N*-hydroxyoxindole.

The degree of conversion 2-(*o*-nitrophenyl)-ethanol as well as the yield of *N*-hydroxyoxindole was influenced by the starting concentration of *1*. They were, however, not influenced by solvent or by the UV light being filtered through pyrex glass, as will be seen from Table 1. The exclusion of oxygen was without effect, and no reaction of compound *1* could be detected by refluxing it in ethanol for 24 h.

During the reaction the solution turned brown. The lowering of the conversion at higher starting concentrations of *1* was probably due to a faster formation of the brown coloured material absorbing the light.

The photochemical redox reaction of 2-(*o*-nitrophenyl)-ethanol was tried under basic condition. If the coloured material was formed by condensation of carboxylic acids with other groups, one could hope that condensation during the irradiation in basic solution might be avoided, thus producing a higher conversion of 2-(*o*-nitrophenyl)-ethanol. However, basic conditions did not give any higher conversion than neutral ones (Table 1).