

## LETTERS TO THE EDITOR

### FORCE FIELDS OF ELECTRONICALLY EXCITED STATES OF SOME TRIATOMIC SYSTEMS

In the  $\bar{X}$  ground state, the molecule HCP and the ion  $N_2O^+$  are both unsymmetrical linear triatomic systems possessing  $C_{\infty v}$  symmetry. When they transform from the  $\bar{X}$  ground state to the electronically excited  $\bar{a}$  state they retain their symmetry and remain linear unsymmetrical. In the excited state the bond lengths are assumed to be the same in the case of HCP; but they vary in the case of  $N_2O^+$ . However, the fundamental vibrational frequencies of both considerably change when they transform from the ground to the excited state<sup>1</sup>. Hence, the force constants and also the behaviour with regard to the other molecular constants like the mean square amplitudes of vibration, Coriolis coupling coefficients and centrifugal distortion constants would change. Thus the normal coordinate analysis of such molecules in the excited states becomes interesting and informative. In the present investigation, the force fields of HCP and  $N_2O^+$  have been studied and the force constants reported.

The four normal vibrations of HCP and  $N_2O^+$  are distributed among two species as  $2\Sigma^+$  and  $1\Pi$ , the frequency under  $\Pi$  species being degenerate.

The molecular parameters and the fundamental vibrational frequencies of HCP and  $N_2O^+$  have been taken from reference 1 and they are presented in

Table I. The force constants of HCP and  $N_2O^+$ , obtained using the general valence and Urey-Bradley force fields, are given in Table II. All the frequencies of the excited state of HCP are less than those of the ground state. Hence the force constants corresponding to the excited state are less than those of the ground state. The bending force constant (H) obtained using Urey-Bradley force field is in contrary to this, due to the negative sign involved in F.

TABLE I

*Molecular parameters and fundamental frequencies of HCP and  $N_2O^+$  in the ground and excited states*

Parameter	HCP		$N_2O^+$	
	Ground state	Excited state	Ground state	Excited state
R (Å)	1.067	1.067	1.155	1.140
D (Å)	1.542	1.542	1.185	1.141
$\alpha$	180°	180°	180°	180°
$\nu_1$ cm <sup>-1</sup>	3216.9	2720	1126.4	1345.5
$\nu_2$ cm <sup>-1</sup>	1278.2	950	1736.6	2451.7
$\nu_3$ cm <sup>-1</sup>	674.3	440	461.2	614

TABLE II

*General valence and Urey-Bradley force constants of HCP and  $N_2O^+$  in the ground and excited states in md/Å*

Molecule	General Valence Force Field			Urey-Bradley Force Field		
	Force constants	Ground state	Excited state	Force constant	Ground state	Excited state
HCP	$f_R$	5.9480	4.1050	$K_R$	5.9610	5.1060
	$f_D$	8.3810	5.1020	$K_D$	8.3940	6.1030
	$f_\alpha$	0.1659	0.0703	H	0.1021	0.1428
	$f_{RD}$	-0.0130	-0.0010	$F^*$	-0.0130	-0.0010
$N_2O^+$	$f_R$	9.2297	11.0363	$K_R$	8.4751	9.7509
	$f_D$	10.3502	24.6198	$K_D$	9.5956	23.3344
	$f_\alpha$	0.2333	0.4352	H	0.1579	0.3067
	$f_{RD}$	0.7546	1.2854	$F^*$	0.7546	1.2854

$F^*$  is the repulsive force constant between the non-bonded atoms.

In the case of  $N_2O^-$  ion, unlike in the case of HCP, the vibrational frequencies increase when the molecule transforms from the ground to excited state. Hence the force constants of  $N_2O^-$  in the excited state are found to be larger than those in the ground state.

In this investigation, we have considered only the  $\bar{a}$  excited state since, this state being the first excited state for both the cases, the relative probability of transformation of the molecules to this state is more when compared to the other higher order excited states.

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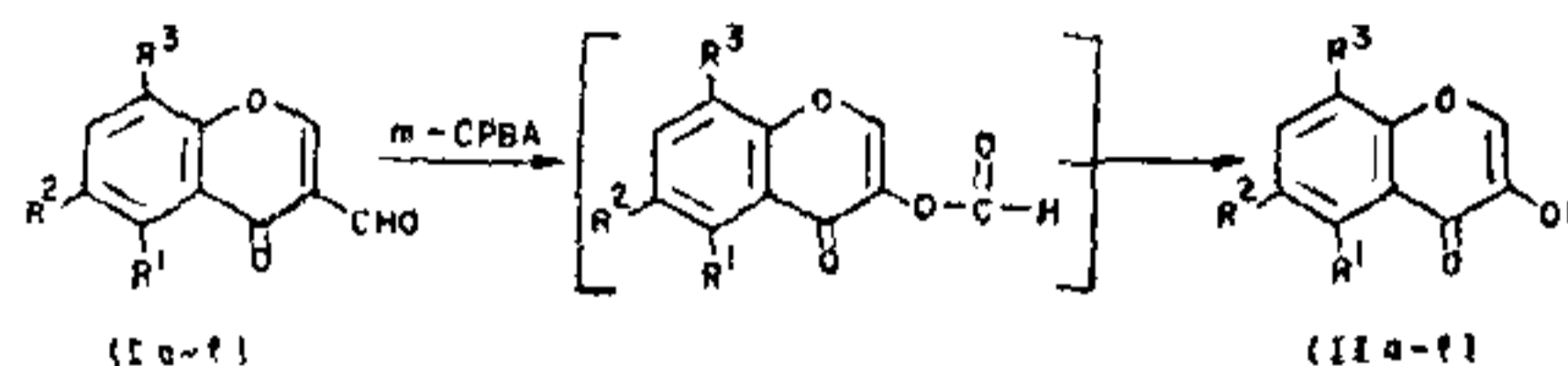
1. Herzberg, G., "Molecular spectra and molecular structure, Part III," *Electronic Spectra of Polyatomic Molecules*, Van Nostrand, New York, 1966, p. 588.

### BAYER-VILLIGER OXIDATION OF CHROMONE 3-CARBOXALDEHYDES— A FACILE METHOD FOR THE SYNTHESIS OF 3-HYDROXYCHROMONES

In this communication we report a facile method for the synthesis of 3-hydroxychromones starting from chromone-3-carboxaldehydes<sup>1,2</sup>. Bayer-Villiger oxidation of methoxybenzaldehydes to methoxyphenols via their respective formates using *m*-chloroperbenzoic acid (*m*-CPBA) in boiling dichloromethane has been recently reported by Sargent *et al.*<sup>3</sup>. Similar procedure has now been adopted for oxidising chromone-3-carboxaldehydes (Ia-e)<sup>1</sup>, (If)<sup>2</sup> to the corresponding 3-hydroxychromones (IIa-c)<sup>4,5</sup> and (IId-f) in good yields, varying from 80-90%. In these reactions, the intermediate formates could not be isolated but the direct formation of 3-hydroxychromones have been observed. The 3-hydroxychromones (IIa-c) thus obtained have been characterised by analytical and spectral characteristics and by direct comparison with authentic samples of IIa<sup>5</sup>, IIb and c<sup>4</sup> respectively (Table I). Also prepared by this new method are 6-chloro (II d), 6-nitro (II e)-3-hydroxychromone<sup>1</sup> and 2-hydroxy-1H-naphtho (2, 1-b) pyran-1-one (II f). These compounds, prepared for the first time, were characterised by analytical and spectral data. II f was also characterised by direct comparison with an authentic sample prepared from 1-benzo (f) chromanone<sup>6</sup> by amylnitrite method<sup>4</sup>.

The overall yield of 3-hydroxychromones (IIa-c and II f) by the present Bayer-Villiger oxidation, calculated from phenol, works out to be ~ 60%, while the yield of the same 3-hydroxychromones prepared by

amylnitrite and hydrochloric acid method<sup>4</sup>, also calculated from phenol, works out to be ~ 16%. Therefore, Bayer-Villiger oxidation method, now reported, appears to be a better method in comparison with the other existing methods<sup>4,5</sup> for the synthesis of 3-hydroxychromones.



- (a)  $R^1 = R^2 = R^3 = H$
- (b)  $R^1 = R^3 = H; R^2 = CH_3$
- (c)  $R^1 = R^2 = H; R^3 = CH_3$
- (d)  $R^1 = R^3 = H; R^2 = Cl$
- (e)  $R^1 = R^3 = H; R^2 = NO_2$
- (f)  $R^1 + R^2 = \text{benzo}; R^3 = H$

#### Experimental

3-Hydroxychromone (IIa)<sup>5</sup>: The chromone-3-carboxaldehyde (Ia)<sup>1</sup> (0.01 mole) and *m*-chloroperbenzoic acid (0.02 mole) were heated under reflux in dry dichloromethane (20 ml) over a period of 16 hours. During reflux a colourless solid (*m*-chlorobenzoic acid) separated out. The reaction mixture was evaporated and the residue dissolved in ethylacetate and the solution washed with aqueous sodium-bicarbonate solution to remove *m*-chlorobenzoic acid and then washed with water and dried over anhydrous sodium sulphate. Removal of the solvent left a solid residue which crystallised from methanol to yield yellowish brown plates of 3-hydroxychromone (IIa), identical in all respects with the authentic sample<sup>5</sup> [(mp, mmp and superimposable ir) (Table I)] prepared by the reported procedure<sup>5</sup>.

IIb and IIc were similarly prepared from their respective chromone-3-carboxaldehydes (Ib and Ic)<sup>1</sup> and were found to be identical with the authentic samples (mp, mmp and superimposable ir), prepared by adopting reported procedures<sup>4,5</sup>.

6-Chloro- (II d)<sup>1</sup>, 6-nitrochromone-3-carboxaldehyde (Ie)<sup>1</sup> and 1H-naphtho (2, 1-b) pyran-1-one-carboxaldehyde (If)<sup>2</sup> on oxidation with *m*-chloroperbenzoic acid yielded 6-chloro-3-hydroxychromone (II d) (found C, 54.98, H, 2.50; calculated for  $C_9H_5OCl$  (C, 55.09, H, 2.55); 6-nitro-3-hydroxychromone (II e) (found C, 52.02, H, 2.40, N, 6.69; calculated for  $C_9H_5O_5N$  C, 52.17, H, 2.42, N, 6.76) and 2-hydroxy-1H-naphthol (2, 1-b) pyran-1-one (II f) (found C, 73.45; H, 3.75; calculated for  $C_{13}H_9O_3$  C, 73.58, H, 3.77) respectively.

II was found to be identical (mp, mmp and superimposable ir) with an authentic sample of 2-hydroxy-1H-naphtho (2, 1-b) pyran-1-one which was prepared by adding a methanolic solution of 1-benzo (f) chroma-