Preliminary Note

The phosphorescent triplet state of several cycloalkanones

R. K. POWER and A. M. NISHIMURA

Department of Chemistry, Wichita State University, Wichita, Kan. 67208 (U.S.A.)

Zero field splittings and the phosphorescence decay rate constants from the triplet excited state of several aliphatic ketones in host matrices are reported. The zero field transitions are not appreciably affected by solvent perturbations, although the phosphorescence relaxation rates vary greatly, depending upon the solvent type.

Since the first observation and characterization of phosphorescence in cyclopentanone, several workers have observed the emission from the n,π^* triplet state in this and other cycloalkanones [1 - 3]. Recently, the use of a fast passage phosphorescence microwave double resonance technique [4] has allowed a more precise determination of the feeding and depopulating parameters in cyclopentanone [5, 6]. Our interest in the cycloalkanones was spurred by the fact that these aliphatic carbonyl molecules consistently yield extremely broad optical spectra with little vibronic structure, whereas aromatic carbonyls such as benzaldehydes and carboxylic acids have phosphorescence emission which possesses well-characterized vibrational features [7, 8]. In order to understand better the electronic relaxation mechanisms via intramolecular and intermolecular interactions, we present some preliminary results on the study of the phosphorescent triplet state in cyclopentanone, cyclohexanone and 1,4-cyclohexanedione.

The three commercially purchased aliphatic ketones were purified by multiple vacuum distillation or sublimation. Single crystals were grown in a Bridgman furnace from zone refined *p*-dichlorobenzene and *p*-dibromobenzene hosts. Research grade *p*-xylene was used without further purification. The experimental details are similar to those of our previous studies [7, 8].

In Table 1 the zero field splittings of the host–guest systems under study are shown along with the total phosphorescence rate constants and relative radiative rates from the individual triplet state sublevels. These relaxation parameters were determined by a rapid passage method outlined by Winscom and Maki [4]. From examination of Table 1, several observations are noteworthy.

(1) In several past studies of the lowest triplet state of benzaldehydes the large zero field splittings observed in several guest–host systems were attributed to spin–orbit contributions to the zero field splittings in the phos-

264

TABLE 1

Zero field transitions in MHz (± 5 MHz), total phosphorescence rate constants in s^{-1} (± 10%) and relative radiative rate constants (± 20%) for several alkanones which were observed at 1.4 K[a]

Guest		Host			
		Pure	p-Xylene	p-Dichlorobenzene	p-Dibromobenzene
Cyclopentanone	Transitions	5022^b	5022^c	5087	5143
		3397	3397	3390	–
		1625	1625	1697	–
	k_z	775	730	300	1000
	k_y	725	730	540	300
	k_x	80	81	66	200
	k_{z_r}	0.47	0.37	–	–
	k_{y_r}	1.0	1.0	1.0	–
	k_{x_r}	0.017	0.018	0.08	–
Cyclohexanone	Transitions	5076	5400	5022	5051
		3367	3611	3364	–
		1752	1792	1645	–
	k_z	400	260	180	6000
	k_y	700	330	1.9	800
	k_x	30	20	39	180
	k_{z_r}	0.02	0.3	100	400
	k_{y_r}	1.0	1.0	1.0	1.0
	k_{x_r}	0.01	0.07	10	–
1,4-Cyclohexanedione[d]	Transitions	2945	–	4539	–
		2223	2184	3074	–
		–	1474	1460	–
	k_z	150	200	330	–
	k_y	440	500	2.0	–
	k_x	37	30	44	–
	k_{z_r}	0.07	0.04	300	–
	k_{y_r}	1.0	1.0	1.0	–
	k_{x_r}	0.02	0.4	20	–

[a] The axes were chosen such that z is along the carbonyl and y is in the plane containing C_2—C_1—C_5.
[b] From ref. 6.
[c] From ref. 6. For cyclopentanone in cyclohexane.
[d] For those entries in which all three transitions were not observed, the energy ordering assignment may not be unique.

phorescent $^3n,\pi^*$ states with a small degree of mixing with a nearby $^3\pi,\pi^*$ state [9]. However, in these ketones where such mixing with $^3\pi,\pi^*$ states is not likely owing to the large energy separation, the zero field splittings for the unperturbed $^3n,\pi^*$ state might be re-examined in the light of these findings.

(2) There is a large difference between the phosphorescence decay rates of the cyclohexanone and of the diketone in the p-xylene host. The smaller rate constants in the chlorinated solvent for the hexylketones could be due either to the enhanced efficiency of the radiative mechanism and the concomitant lowering of the non-radiative relaxation route and/or to a pseudo Jahn–Teller type interaction which is absent in the p-xylene and in the pure crystals [8]. The coupling of the electronic relaxation mechanisms to vibrational modes of aliphatic ketones has been well established [2, 3, 10]. Whether or not the hexylketones are distorted in p-dichlorobenzene such that the non-totally symmetric vibrations are not coupled as effectively is a question open to further study. The fact that phosphorescence emission was not observed for 2-adamantanone in our initial study might be further evidence that these out-of-plane vibrational motions are essential to the electronic relaxation mechanisms for aliphatic ketones.

(3) The second order external heavy atom contribution to the zero field splitting in the $^3n,\pi^*$ state of the aliphatic ketones is very small. The contribution appears to be less than about 2%. This finding is similar to conclusions drawn from studies on the $^3\pi,\pi^*$ phosphorescent states in aromatic molecules such as quinoxalines [11, 12], quinolines [13] and naphthalenes [12, 13].

In an effort to understand the reasons for the extremely broad optical emission lines in these cyclic ketones, "hole burning" experiments in the zero field transition line were attempted [14]. Our preliminary negative results might be interpreted to indicate that the linewidth is homogeneously broadened by non-specific substitution of the guest molecule in the host crystals. An alternative explanation might be that the stationary microwave field did not saturate the transition owing to the lack of power. (That rapid interchange of several multiconfigurational forms in these cyclic ketones exists even at 1.4 K as suggested by Shain and Sharnoff [15, 16] might have been an alternative explanation. Recent work, however, has shown that the rate of inversion tunnelling is either very slow or does not occur [17].)

It should be noted in passing that in the attempted hole burning experiments, a careful analysis of the microwave frequencies with a spectrum analyzer showed several intense spurious signals. In addition, the modulation of one of the microwave oscillators with a PIN diode was found to cause the modulation to alternate between the two oscillator frequencies. Thus when the phosphorescence signals are phase locked against a reference frequency equal to the amplitude modulation, false resonances are observed which are out of phase with respect to the true transition. The resulting spectrum is similar to those reported by other workers who interpreted the spectrum as having been caused by inversion tunnelling [15, 16].

To obtain further information regarding the role of vibronic activity of the α hydrogens in the electronic relaxation mechanisms, we are currently examining the effects of isotopic substitution of the α hydrogens in the cyclic alkanones. The effects of intermolecular relaxation mechanisms for these molecules are also being further examined.

1 S. R. LaPaglia and B. C. Roquitte, J. Phys. Chem., 66 (1962) 1739.
2 M. O'Sullivan and A. C. Testa, J. Am. Chem. Soc., 92 (1970) 258.
3 W. D. Chandler and L. Goodman, J. Mol. Spectrosc., 35 (1970) 232.
4 C. J. Winscom and A. H. Maki, Chem. Phys. Lett., 12 (1971) 264.
5 A. L. Shain, W. T. Chiang and M. Sharnoff, Chem. Phys. Lett., 16 (1972) 206.
6 A. L. Shain and M. Sharnoff, Chem. Phys. Lett., 16 (1972) 503.
7 A. M. Nishimura and D. S. Tinti, Chem. Phys. Lett., 13 (1972) 278.
8 K. A. Martin, G. Moller and A. M. Nishimura, J. Phys. Chem., 80 (1976) 2788.
9 M. A. El-Sayed, Double resonance and the properties of the lowest excited triplet state of organic molecules, in Annu. Rev. Phys. Chem., 26 (1975) 235 - 258.
10 M. O'Sullivan and A. C. Testa, J. Am. Chem. Soc., 92 (1970) 5842; J. Lumin., 10 (1975) 123.
11 S. Yamaguchi, K. Matsuzaki and T. Azumi, J. Lumin., 12/13 (1976) 369.
12 C. T. Lin, J. Lumin., 12/13 (1976) 375.
13 K. J. Latas and A. M. Nishimura, submitted for publication.
14 M. Leung and M. A. El-Sayed, Chem. Phys. Lett., 16 (1972) 454.
15 M. Sharnoff and A. L. Shain, J. Am. Chem. Soc., 95 (1973) 6465.
16 A. L. Shain and M. Sharnoff, Chem. Phys. Lett., 22 (1973) 56.
17 M. E. Tarrash, C. R. Chen and C. B. Harris, Chem. Phys. Lett., 48 (1977) 579.