



Present address of Dr. Zhongping Lin:
Batelle Research Institute, 505 King Ave.
Columbus, OH 43201-2693 USA

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Triplet-state energies and substituent effects of excited aroyl compounds in the gas phase[☆]

Zhong-Ping Lin *, Walter A. Aue

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, B3H 4J3, Canada

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Abstract

Triplet-state energy values obtained from the gas phase are still scarce. In this study, the triplet-state energies of 58 aroyl compounds, introduced as gas chromatographic peaks at atmospheric pressure and typically 473 K, have been determined from the 0–0 bands of their $n \rightarrow \pi^*$ type phosphorescence spectra in excited nitrogen. Correlations of those gas-phase triplet-state energies with Hammett constants could be observed for substituted acetophenones, benzaldehydes and benzophenones. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Triplet-state energies; Gas phase; Aroyl compounds; Phosphorescence; Hammett constant

1. Introduction

One particularly intriguing aspect of photochemical studies deals with the electronic energy levels of excited molecules. Knowledge of the intermolecularly transferred electronic energy has been important in finding new photochemical reactions: this energy plays a major role in directing their course, and it thus helps in elucidating their mechanism. So-called triplet–triplet energy transfer is the most common and the most important

type of excitation in organic photochemistry [1,2]. Knowing the electronic energy levels of a compound may permit it to be used as either a photosensitizer (donor) or as a quencher (acceptor) in photochemical studies. For a successful selection of photosensitizers and quenchers, it is necessary to have available a series of compounds with triplet energies distributed over a wide range.

A number of triplet state energies have been reported in the literature [3]. However, most of these values were measured in condensed phases. It is well known that solvent effects may change the nature of the lowest excited state [4] and cause significant spectral shifts [5]. Thus discrepancies occur in the literature among the values of triplet energies according to solvent or solid matrix. Accurate values of triplet-state energies from the gas phase would be preferable, but such values are still scarce.

[☆] From the doctoral thesis of Z.P. Lin, Dalhousie University, 1997.

* Corresponding author.

The present study should help to alleviate this problem. A novel, radioactively stimulated, high-voltage, low-current DC discharge in high-purity nitrogen was operated in a gas chromatographic environment. Under these circumstances, certain types of aroyl compounds produced strong gas-phase luminescence. The luminescence consisted

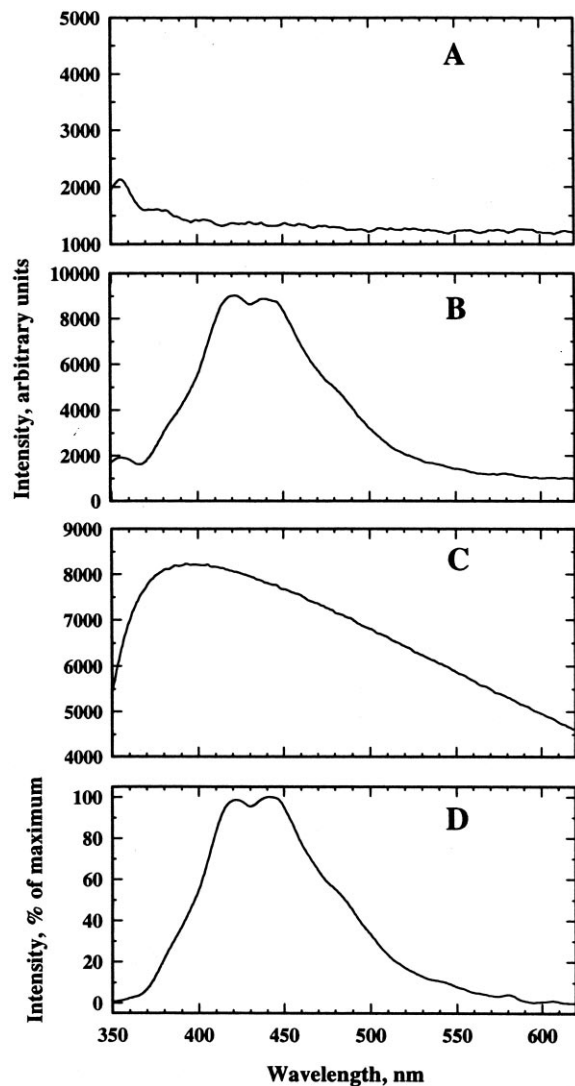


Fig. 1. Typical example of traces used for obtaining a referenced aroyl spectrum. (A) Background spectrum in the ALD. (B) Raw spectrum of benzophenone from the dispersive channel. (C) Chromatographic signal from the nondispersive channel. (D) Referenced gas-phase luminescence spectrum of benzophenone.

of typical $n \rightarrow \pi^*$ excited, triplet \rightarrow singlet emission spectra as found in conventional phosphorescence; however, here they were produced by gas-phase energy transfer from—most likely—metastable N_2 ($A^3 \Sigma_u^+$) [6]. The gas-phase phosphorescence of aroyl compounds in excited nitrogen is easy to measure: in analytical terms, less than 1 pg of a strong emitter can be quantified. In this manner, the triplet-state energy levels of gas-phase molecules can be determined without much difficulty.

2. Experimental

The luminescence measurements were made in one or more of the different spectral acquisition modes available on the gas chromatographic aroyl luminescence detector (ALD) [6]. The ALD is an analytical and spectral device constructed to capitalize on earlier studies of this phenomenon in our lab [7]. For strongly luminescing compounds such as benzaldehyde, the gas-phase spectrum was obtained with a Jarrell–Ash model 82-415 quarter-meter monochromator and/or an Oriel model 77 250 eighth-meter monochromator. The spectra obtained by the two monochromators were identical, except for the different intensity distributions due to the distinctly different light transmission profiles of the two gratings. In most cases, spectra were recorded by the single-peak mode [8]. Such spectra originate from scanning a single chromatographic peak during its passage through the triple-channel ALD system [6], usually with the help of the eighth-meter monochromator. (For some weakly emitting compounds such as 1,4-naphthoquinone, a low-resolution device with a far greater light throughput, the Oriel model 7155 filter monochromator, was used with manual adjustment of wavelength between repeated sample injections.)

In order to obtain accurate and either highly sensitive or highly resolved spectra in the single-peak mode, more than 10 ng of a well-luminescing aroyl compound had to be injected into the gas chromatograph. However, spectra could still be measured from a peak of less than 10 ng, though at some loss in resolution. In practice, aroyl

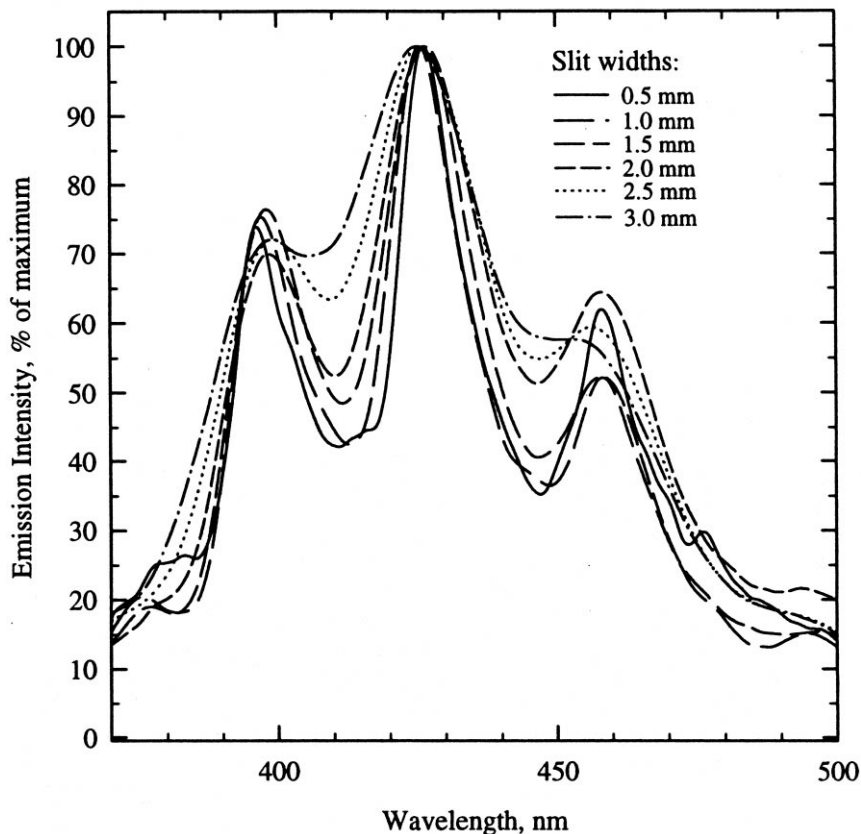


Fig. 2. Gas-phase luminescence spectrum of benzaldehyde in excited nitrogen obtained from a 100 ng peak with the 1/8 meter grating monochromator, an R-374 PMT, and different slit widths.

amounts corresponding to the upper end of their linear calibration range were introduced into the ALD. A weak background spectrum from pure nitrogen [the so-called second positive system, $N_2(C^3\Pi_u) \rightarrow N_2(B^3\Pi_g)$] persisted in the ALD (Fig. 1A). In order to obtain accurate spectral information, this nitrogen background had to be deducted from the raw spectrum of the dispersive channel (Fig. 1B). Also, the aroyl concentration profile (the rise and fall of the chromatographic peak) had to be taken into account. The net raw spectrum (1B–1A) was therefore divided by the chromatographic peak profile (Fig. 1C). These corrections were easy to implement, either by a suitable algorithm as found in the CHROM 8 program [9], or on a spreadsheet. The thus referenced sample spectrum of benzophenone is shown in Fig. 1D; it is typical for most spectra measured

in this study. However, none of these referenced spectra were corrected for photomultiplier quantum yield, monochromator grating efficiency, or other instrumental variables. Only the crucial wavelength indicator of the monochromator was recalibrated from time to time by using the mercury lines.

As a further typical illustration, Fig. 2 shows the (referenced) gas-phase luminescence spectrum of benzaldehyde, measured by using the 1/8 meter monochromator with different slit widths. Under the specific ALD conditions (atmospheric-pressure nitrogen at the elevated temperatures typical of gas chromatographic detection), the spectral resolution did not improve much below a given slit width. In other words, the broadness of the bands was due to the fact that at high temperature and pressure the population of upper vibra-

Table 1
Triplet state energies of some aroyl compounds

Compound	Experimental value ($E_T(g)$) (kJ mol ⁻¹) ^a	Literature value (kJ mol ⁻¹)			Reference		
		$E_T(g)$ ^b	$E_T(n)$ ^c	$E_T(p)$ ^d	$E_T(g)$	$E_T(n)$	$E_T(p)$
Benzaldehyde	301	301	301	298	[10]	[3]	[3]
Isophthalaldehyde	298						
Terephthal-dicarboxaldehyde	286		277			[3]	
3-Methylbenzaldehyde	300		302			[3]	
4-Methylbenzaldehyde	303		305	298		[3]	[3]
4-Ethylbenzaldehyde	302						
4-Isopropylbenzaldehyde	301						
2-Fluorobenzaldehyde	293		295			[3]	
3-Fluorobenzaldehyde	298		299			[3]	
4-Fluorobenzaldehyde	304	304	305		[11]	[3]	
2-Chlorobenzaldehyde	288		290			[3]	
4-Chlorobenzaldehyde	299	299	300		[11]	[3]	
2,6-Dichlorobenzaldehyde	290						
3-Cyanobenzaldehyde	295						
4-Cyanobenzaldehyde	288						
4-Acetoxybenzaldehyde	302						
3-Methoxybenzaldehyde	300						
4-Methoxybenzaldehyde	304	309	300	295	[12]	[3]	[3]
4-Ethoxybenzaldehyde	304						
Methyl-4-formylbenzoate	292						
Ethyl-4-formylbenzoate	292						
1-Chloroethyl-4-formylbenzoate	292						
1,1,1-Trifluoroethyl-4-formylbenzoate	292						
<i>n</i> -Heptyl-4-formylbenzoate	293						
Benzophenone	285	285	287	289	[12]	[3]	[3]
4-Methylbenzophenone	285		287	290		[3]	[3]
4-Methoxybenzophenone	288		287	290		[3]	[3]
3,3'-Bis(trifluoromethyl)benzophenone	283		280	289		[3]	[13]
4-Chlorobenzophenone	285		286	288		[3]	[3]
2-Chlorobenzophenone	285						
4,4-Dichlorobenzophenone	283		285	286		[3]	[3]
2-Benzoylpyridine	272		279	282		[3]	[3]
3-Benzoylpyridine	285		286	288		[3]	[3]
4-Benzoylpyridine	279		281	281		[3]	[3]
4-Benzoylbiphenyl	260			254			[3]
Acetophenone	304	304	310	311	[12]	[3]	[3]
3'-Methylacetophenone	304		306	303		[3]	[3]
4'-Methylacetophenone	305		305	305		[3]	[3]
4'-Fluoroacetophenone	305						
3-Acetylbenzoxirone	296		295	307		[3]	[3]
4-Acetylbenzoxirone	290		290	291		[3]	[3]
2-Acetylpyridine	289		293	296		[3]	[3]
4-Acetylpyridine	292		290	295		[3]	[3]
Anthraquinone	264	264	261	263	[14]	[3]	[3]
2-Methylanthraquinone	265		261			[15]	
2-Ethylanthraquinone	265						
1-Chloroanthraquinone	265		262			[15]	
Benz(g)isoquinoline-5,10-dione	265						

Table 1 (continued)

1,4,4a,9a-Tetrahydroanthraquinone	265				
Anthrone	302		301		[3]
Xanthrone	306		310	310	[3]
Thio-xanthene-9-one	315 ^c		265		[3]
9-Anthraldehyde	279 ^c		182		[16]
α -Tetralone	299		303	304	[3]
1,4-Naphthoquinone	246	245		241	[17]
2-Methyl-1,4-naphthoquinone	244	244			[17]
<i>trans</i> -Cinnamaldehyde	300				
Dibenzosuberone	270				

^a Determined from the 0–0 band of the phosphorescence spectra.

^b Triplet state energy measured in the gas phase.

^c Triplet state energy measured in non-polar solvent.

^d Triplet state energy measured in polar solvent.

^e Phosphorescence origin questionable.

tional energy levels was enhanced, and that the rotational sub-levels were so closely spaced as to form a near continuum. Based on this fact, the slit width for luminescence measurements was usually set to 2 or 1 mm. The scan rate was 300 nm min⁻¹, to keep up with the (deliberately broadened) gas chromatographic peak.

3. Results and discussion

Triplet energies are commonly estimated from the 0–0 band in singlet–triplet absorption spectra, from the 0–0 band in phosphorescence spectra, or from energy titration via triplet–triplet energy transfer. Phosphorescence is the most widely used of these three methods and gives the most definitive values. The triplet state energies listed in Table 1 were calculated from the highest-energy (i.e. 0–0 band) maximum in the respective phosphorescence spectra. According to the Frank–Condon principle [2], if the triplet and ground states have significantly different geometries, the 0–0 band may not be the band of maximum intensity. As is well known, some aroyl compounds such as benzophenones and anthraquinones emit not only phosphorescence from a triplet n, π^* state, but also weak E-type delayed fluorescence. In order to calculate triplet state energies, the 0–0 phosphorescence band must therefore be correctly identified. For most phospho-

rescence spectra, such as those of the benzaldehydes, little difficulty was encountered in

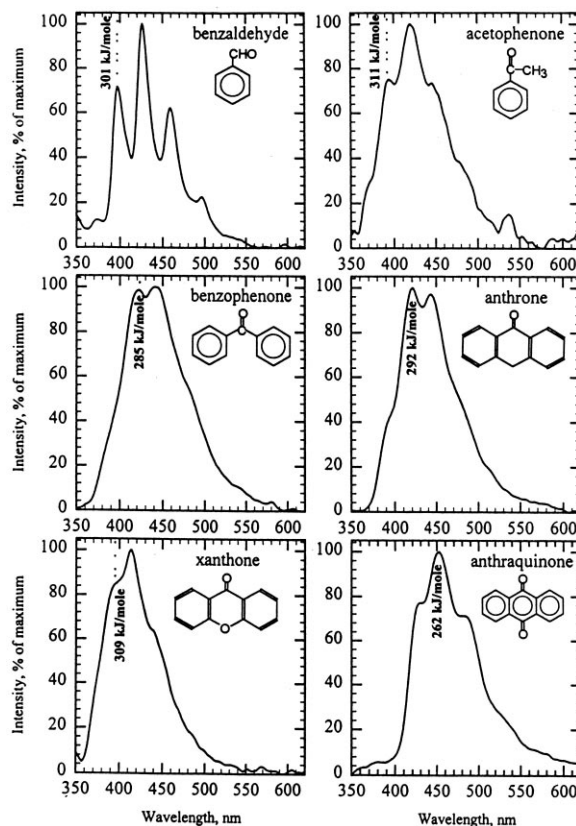


Fig. 3. Gas-phase luminescence spectra of some typical aroyl compounds obtained by the single-peak mode.

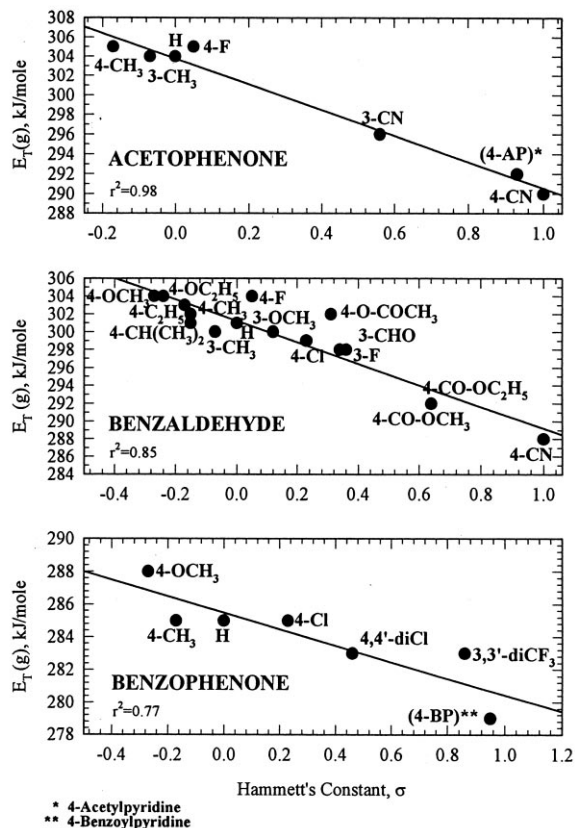


Fig. 4. Substituent effects on the triplet energy (0–0 band) of substituted acetophenones, benzaldehydes and benzophenones in the gas phase.

assigning the 0–0 band, since vibronic structure was usually well developed. In some other cases, however, e.g. those of xanthone and some substituted acetophenones, the broadness of the bands made the precise assignment of the 0–0 band position more difficult. Typical working examples of gas-phase phosphorescence spectra, including some difficult ones, are shown in Fig. 3.

As can be seen from Table 1, our gas-phase values differ slightly from the literature values measured in *condensed* phases. Literature data from the gas phase, however (where such exist), are nigh identical with those obtained in excited nitrogen during this study. There is only one minor discrepancy, i.e. that of 4-methoxybenzaldehyde, between the spectra of this study and the nine cases of gas-phase spectra available from the literature.

It was found, not unexpectedly, that the n, π^* triplet state energies of substituted aroyl compounds correlate with typical substituent effects in reactions. Generally, and for a given series, electron-donating substituents increase, while electron-withdrawing substituents decrease, the n, π^*

triplet state energy. This correlation is illustrated in Fig. 4, in which the triplet state energies of substituted acetophenones, benzaldehydes and benzophenones are plotted against the Hammett substituent constant σ ; [3,18,19]. A similar correlation was observed for the triplet state energies from condensed phases [20]. The effect of substituents on the n, π^* triplet state energy has been rationalized in terms of charge redistribution between the ground and excited states [13,21], in which the electron density on oxygen decreases upon excitation [5,22].

In contrast to the groups of compounds shown in Fig. 4, the substituent effect is not pronounced in anthraquinones. This means that adding substituents does little to alter the character of triplet states intrinsic to the unsubstituted anthraquinone molecule.

4. Conclusions

Intense gas-phase phosphorescence at atmospheric pressure and high temperature (typically 473 K) is an unusual phenomenon. In this study, the easily detectable gas-phase phosphorescence of aroyl compounds in excited nitrogen permitted us to measure the triplet-state energies of some 58 compounds, 49 of which had not been measured before in the gas phase. It was found that, for a given series, electron-donating substituents increase, while electron-withdrawing substituents decrease, the n, π^* triplet state energy.

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