Origin of the Anomalous Phosphorescence of 1-Indanone and Related Ketones

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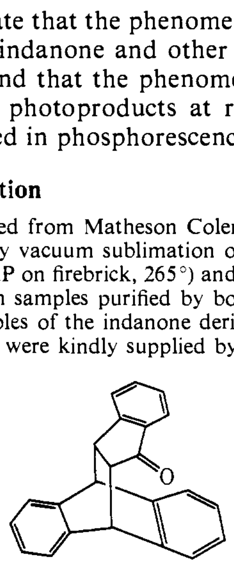
Abstract: The phenomenon of dual phosphorescence from 1-indanone, 1-tetralone, and I has been investigated using various spectroscopic techniques, including absorption, phosphorescence, and phosphorescence excitation spectroscopy. From these studies we demonstrate that the "anomalous" long-lived emission observed from 1-indanone, 1-tetralone, and I is due to photoproducts which are formed at room temperature and then observed in phosphorescence at 77°K. Other possible interpretations of the phenomenon are shown to be incorrect.

Five years ago Yang and Murov reported that 1-indanone exhibits two groups of phosphorescence which could be spectrally resolved simply by varying the chopper speed of the phosphoroscope.[1] These authors assigned the short-lived (1.5–2 msec) emission to emission from the $^3(n,\pi^*)$ state of indanone. The long-lived emission (0.15–0.2 sec) was assigned to an indanone triplet state with mixed n,π^* and π,π^* character, but no suggestion as to the origin of the phenomenon was given. Dual phosphorescence can also be observed from other aromatic ketones,[1–4] and in a recent paper, Kanda, Stanislaus, and Lim have carried out a detailed examination of the phosphorescence of 1-indanone and related compounds.[5] On the basis of this study they proposed that the long-lived emission was due to the reversible photochemical formation of the enolate anion in its triplet state. The short-lived emission was correspondingly attributed to emission from the $^3(n,\pi^*)$ state of 1-indanone. In support of this proposal they noted the following facts. The long-lived emission is stronger in the more polar solvents where the enolate ion would be more stable. The excitation spectra of the long- and short-lived emissions are very similar (but not identical) and this was interpreted as indicating that the enolate ion was formed in its excited triplet state by excitation of 1-indanone. 1-Tetralone and 2,2-dimethylindanone were reported not to exhibit dual phosphorescence in accord with the lowered acidity or absence of hydrogen atoms at the 2 position. Additional evidence for the formation of the enolate anion of 1-indanone was subsequently provided by an nmr investigation of the photoinduced exchange of the 2-position protons of 1-indanone in polar (CH_3OD) solvent.[6]

With 1-indanone the lifetimes of the two different emissions are so different that it has been relatively simple to spectrally resolve these two emissions. In the case of other ketones, however, where the spectra are less well resolved, and where the lifetimes are more similar, it may be much more difficult to show that there are actually two different emissions present. In this case, dual phosphorescence would only be manifested by nonexponential decay of the phosphorescence. Since nonexponential phosphorescence decay has now been observed from a number of different carbonyl-containing compounds, the interpretation of the dual phosphorescence of 1-indanone might have very wide applicability.[7,8] Because of this and our interest in the spectroscopic properties of various ketones and enones,[9–11] we have reexamined the phosphorescence of 1-indanone. On the basis of this study we have been able to demonstrate that the phenomenon of dual phosphorescence in 1-indanone and other aromatic ketones is quite general and that the phenomenon results from the formation of photoproducts at room temperature which are observed in phosphorescence at 77°K.

Experimental Section

1-Indanone obtained from Matheson Coleman and Bell (MCB) was purified either by vacuum sublimation or by gas chromatography (3-ft 20% FFAP on firebrick, 265°) and the phosphorescence results obtained from samples purified by both methods were the same. Purified samples of the indanone derivative I, whose structure is shown below, were kindly supplied by Dr. Kurt Schaffner.



I

1-Tetralone obtained from MCB was purified by vaccuum fractional distillation. Pinacols of 1-indanone were prepared by chemical reduction with aluminum metal[12] and purified by passing through a silica gel column using ether as the eluent. The solvents used were commercially available spectroscopic grade.

Phosphorescence and phosphorescence excitation spectra were measured by a standard phosphorimeter (6-mm diameter sample tube) with a rotating can. Unless stated otherwise, the excitation wavelength was ~296 nm.

With a fast chopper speed the interval between excitation and observation of the emission is 10 msec, and with a slow chopper speed the interval is about 40 msec. Triplet state lifetimes were measured using a Xe flash lamp (0.25-msec duration) to excite the

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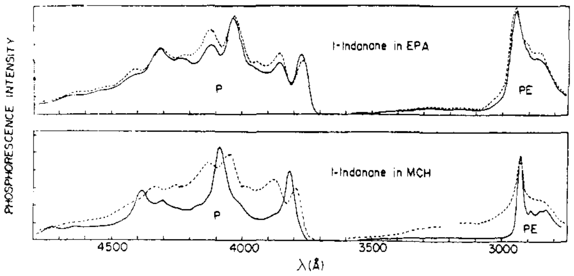

Figure 1. The 77°K phosphorescence (P) and phosphorescence excitation (PE) spectra of 1 × 10^{-4} *M* 1-indanone solution in EPA, methylcyclohexane (MCH) at fast (——) and slow (- - -) chopper speeds.

samples (exciting light filtered with a Corning 7-54 filter). The phosphorescence emission was monitored through appropriate interference filters by an RCA 1P28 photomultiplier and the resulting signal was displayed on a Tektronix 545A oscilloscope and photographed. Absorption spectra were measured with a Cary 14 spectrophotometer. Spectral grade solvents were used without further purification since they exhibited no detectable emission under the conditions we used to monitor the ketone emission.

Results and Discussion

The 77°K phosphorescence and phosphorescence excitation spectra of 1 × 10^{-4} *M* 1-indanone solution in EPA at fast and slow chopper speeds are illustrated in Figure 1. It is clear from Figure 1 that the emission spectrum changes with chopper speed. Although the excitation spectra of long- and short-lived emissions are similar, the shoulder at 300 nm becomes stronger at the slower chopper speed. These observations simply reconfirm the results previously reported by Yang and Murov[1] and by Kanda, Stanislaus, and Lim.[5]

The 77°K phosphorescence and phosphorescence excitation spectra of 1 × 10^{-4} *M* 1-indanone solution in methylcyclohexane (MCH) have also been measured at different chopper speeds and these results are shown in Figure 1. It is important to the later discussion to note that the origin of the long-lived phosphorescence (379.5 nm) is higher in energy than the origin of the short-lived phosphorescence. The excitation spectrum of the short-lived phosphorescence (when corrected for the variation in the photon intensity with wavelength) is identical with the absorption spectrum of 1-indanone; however, the excitation spectrum of the long-lived component has relatively more intensity in the $^1(n,\pi^*)$ absorption region (300–350 nm). The lifetime of the short-lived component is 1.4 msec, while that of the long-lived component is on the order of 0.1 sec.

Entirely similar results are also obtained for I and 1-tetralone and these are presented in Figure 2.

The current interpretation of dual phosphorescence is due to Kanda, Stanislaus, and Lim.[5] They propose that the long-lived emission of 1-indanone arises from enolate anions which are formed in their *excited* triplet states as a result of excitation of *ground* state indanone molecules. This accounts for the fact that the excitation spectra of both the long- and the short-lived emissions are similar and for the apparent solvent dependence of the effects. It would appear, however, that this suggestion can be ruled out simply from energetic considerations.[13] In normal solvents (*i.e.*, MCH and EPA) the enol and enolate forms of indanone are thermodynamically unstable with respect to the keto form. In the excited state, however, Kanda, *et al.*, propose that because of an increase in acidity, the enolate triplet state is as stable or more stable than the n,π* triplet state of the keto form (see Figure 9, ref 5). A necessary consequence of these energetic considerations is that the phosphorescence origin of the enolate ion should be at *lower* energy than the emission from the $^3(n,\pi^*)$ state of the keto form. As we noted above, exactly the opposite result is observed experimentally; the origin of the long-lived emission is at higher energy than the short-lived emission. This discrepancy in energy, coupled with the observation of dual phosphorescence from both 1-tetralone and I, demonstrates that the Kanda–Stanislaus–Lim interpretation of the dual phosphorescence of 1-indanone is not correct and that some other explanation must be found.

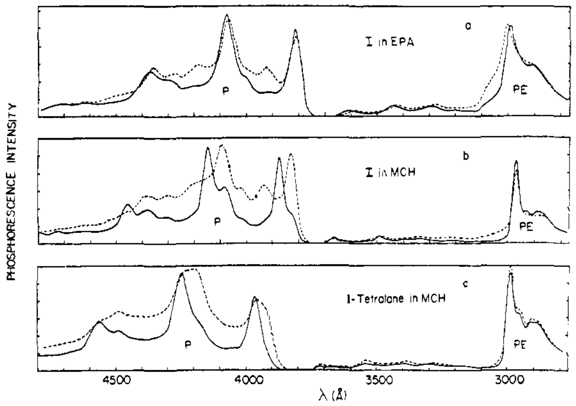

Figure 2. The 77°K phosphorescence (P) and phosphorescence excitation (PE) spectra of (a) 3 × 10^{-4} *M* I in EPA, (b) 5 × 10^{-5} *M* I in MCH, and (c) 3 × 10^{-4} *M* 1-tetralone in MCH at fast (——) and slow (- - -) chopper speeds.

Since the lowest n,π* and π,π* triplet states of crystalline 1-indanone are nearly degenerate in energy (within 260 cm^{-1}),[14] it was possible that the ordering of these two states in solution might depend very sensitively on the local molecular environment. Dual phosphorescence would then arise simply from the presence of two different types of molecular environments, one in which the $^3(\pi,\pi^*)$ state is lowest in energy and the other in which the $^3(n,\pi^*)$ state is lowest. Kanda, *et al.*, rejected this notion on the basis that the phenomenon could be observed in single component solvents where the solute environments must be reasonably uniform. Although work with Shpolskii glasses demonstrates that this is not necessarily correct,[15] other data discussed below show that the "two site" proposal is incorrect. Thermal equilibration between two nearly degenerate triple states offered another possible explanation for the occurrence of dual phosphorescence at 77°K, but this fails to account for the fact that the two different emissions have very different lifetimes. Furthermore, we were able to observe both the long- and short-lived emissions at 4.2°K where the emission from the higher energy component should have been completely "frozen" out.

There were certain indications that the dual phosphorescence might be due to the formation of dimers, and we accordingly checked this possibility by examining the

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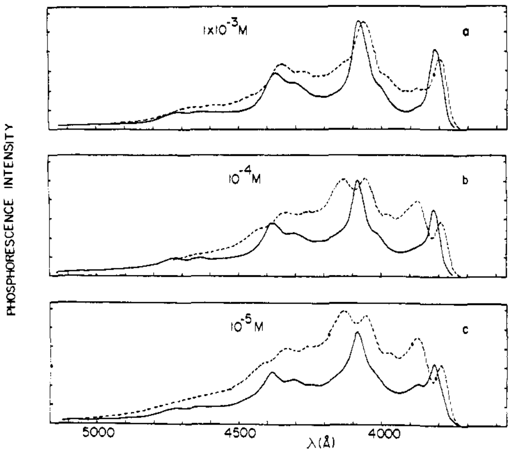

Figure 3. The 77°K phosphorescence spectra of 1-indanone in MCH at various concentrations. Solid line is for fast chopper speed and dashed line is for slow chopper speed.

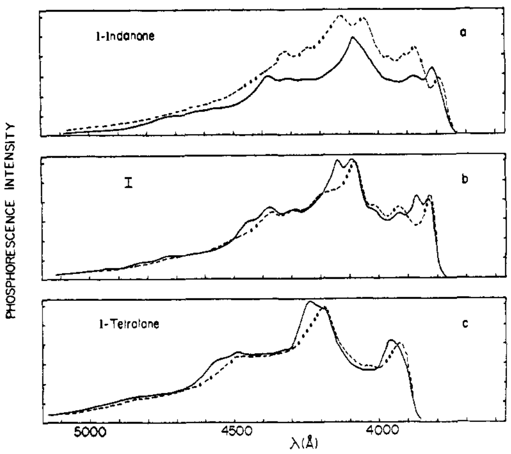

Figure 5. The 77°K phosphorescence spectrum of (a) 1 × 10^{-4} *M* 1-indanone, (b) 5 × 10^{-5} *M* I, and (c) 3 × 10^{-4} *M* 1-tetralone in MCH at fast (——) and slow (- - -) chopper speeds after 30 sec of irradiation at 295°K.

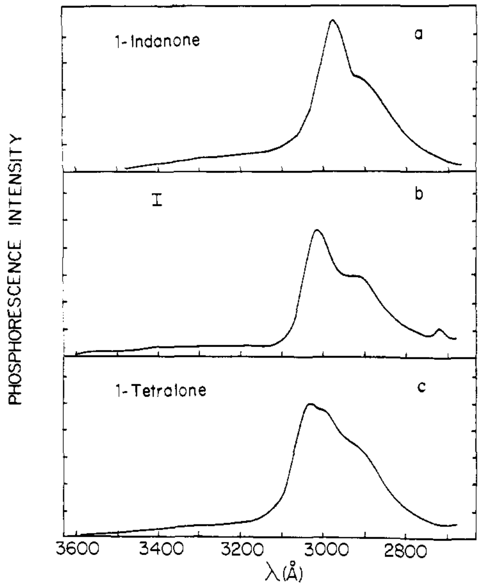

Figure 4. The 77°K phosphorescence excitation spectra (slow chopper speed) of (a) 1 × 10^{-4} *M* 1-indanone, (b) 5 × 10^{-6} *M* I, and (c) 3 × 10^{-4} *M* 1-tetralone in MCH. (a) and (c) are obtained after 30 sec of irradiation at 295°K.

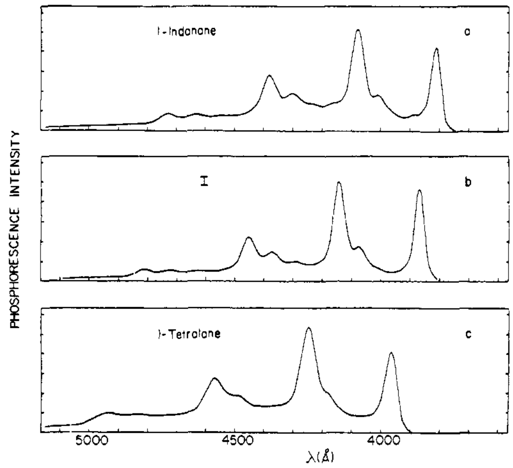

Figure 6. The authentic phosphorescence spectrum of (a) 1-indanone, (b) I, and (c) 1-tetralone in MCH at 77°K.

emission spectrum of 1-indanone at different concentrations in MCH and these results are illustrated in Figure 3. Entirely similar results were obtained with I and 1-tetralone. These results clearly indicate that the emission characteristics of all three compounds are very sensitive to concentration. In particular, it is important to note that the long-lived component is always strongest in the most dilute solutions and that it is virtually absent at high concentrations. Furthermore, the excitation spectrum of the long-lived emission from a 5 × 10^{-6} *M* compound I solution in MCH which is shown in Figure 4 is diffuse and red-shifted relative to the excitation spectrum of the short-lived emission. Since the long-lived emission is strongest in dilute solutions it would be reasonable to assign this as emission from monomers and to assign the short-lived emission as emission from dimers or higher aggregates. Such an assignment is ruled out by the observation that it is the excitation spectrum of the short-lived component, not the long-lived component, which is identical with the absorption spectrum of dilute solutions of compound I. Furthermore, there is no evidence for a band in the absorption spectrum corresponding to the 316-nm band observed in the excitation spectrum of the long-lived component. Therefore, the formation of dimers and higher aggregates cannot explain dual phosphorescence.

Since aromatic ketones are known to undergo photoreduction when irradiated at room temperature,[16] it was possible that the long-lived emission might be due to products of such a photoreduction. In order to test this proposal we examined the effect of *room* temperature irradiation on the low-temperature emission properties of a carefully prepared solution of 1-indanone (1 × 10^{-4} *M*) in MCH. Before irradiation at room temperature, the short-lived $^3(n,\pi^*)$ emission was very strong, and the long-lived component was barely detectible. However, after only 30 sec of irradiation (Bausch and Lomb SP-200 Hg lamp), the long-lived component became much stronger than the short-lived component. The intensity of the long-lived emission increases to a maximum after only 1 min of irradiation

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[16] See, for example, J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966.

at room temperature (see Figure 5) but with further irradiation the emission intensity decreases. The samples appeared to be photochemically stable at 77°K. The excitation spectrum of the long-lived emission which we purposely generated photochemically was identical with that observed in the other 1-indanone samples. Entirely similar photochemical effects are observed for I as well as 1-tetralone as the results shown in Figure 5 demonstrate. These observations with I and 1-tetralone appear to confirm the generality of this effect. The fact that Kanda, *et al.*,[5] did not observe long-lived emission from 1-tetralone might simply be due to their choice of concentrations.

We have attributed the short-lived emissions of 1-indanone, I, and 1-tetralone to emission from a $^3(n,\pi^*)$ state. Since the emission spectra which have been published before have been mixtures of short- and long-lived components, we have presented in Figure 6 emission spectra which were obtained under conditions such that the long-lived component is either absent or negligible. We have shown that the long-lived emissions are due to photoreduction products which are generated at room temperature, but we have not identified these photoproducts. Although pinacols are the major photoreduction products from 1-indanone,[13] these compounds are not phosphorescent. It is possible, however, to observe the long-lived emission from pinacol solutions if they are first irradiated for 30 sec at room temperature. The excitation spectrum of the long-lived phosphorescence (weak bands extending out to about 355 nm) indicates that emitting species still contain a carbonyl group conjugated with the aromatic ring, but beyond this we have no further information about the nature of the phosphorescent products.

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Reduction of the Mercuric Ion Induced by the Photolysis of the Uranyl–Organic Systems

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Abstract: Reduction of the mercuric ion induced by the photoredox reactions of the uranyl–organic systems has been studied both in aqueous and in 10% polyvinyl alcohol (PVA) solutions with the irradiation of $\lambda \geq 3650$ Å at room temperature. It appeared that the mercuric ion was reduced by the intermediate species formed in the primary photoredox reaction between the excited uranyl ion and ethanol. The formation of the uranium(IV) was completely inhibited by the mercuric ion, while acetaldehyde formation was not retarded. The molar ratios were $[U(IV)]/[aldehyde] = 0$, and $-\Delta[HgCl_2]/[aldehyde] = 2$, for the deoxygenated aqueous solutions. The reaction in the viscous PVA solution led to a uniform suspension of mercurous chloride, and the change in its optical density was followed with the time of irradiation. The mercuric reduction was also found in the photoredox reactions of other systems than the ethanol–uranyl system. The high photosensitivity suggested utility for a photographic process.

In the course of the study of the inhibitory effects on the photolysis of the uranyl–organic systems, the mercuric ion was found to be a highly sensitive and selective scavenger of the intermediates. When a 20% aqueous alcohol solution containing 0.005 *M* mercuric chloride and 0.01 *M* uranyl nitrate was exposed to visible light for 10 sec using a 500-W incandescent lamp, there appeared a turbidity and the transmittance of the solution fell below 10% (per 1 cm depth), which was not observed in the absence of either the uranyl ion or alcohols. The high photosensitivity was retained in the viscous polyvinyl alcohol (PVA) solution, suggesting its utility for a photographic process. Recently, the self-quenching reaction of the uranyl ions in a polymer solution has been reported,[1] while photographic properties of polymeric mercurous compound have been studied.[2]

In the present work the reduction of the mercuric ion by the intermediate species formed in the photolysis of the uranyl–organic systems was investigated and a preliminary examination on the possible application to photographic purposes was made.

Experimental Section

Doubly distilled water and guaranteed reagents were used, while polyvinyl alcohol was chemical grade (Kanto Chemicals No. 500, No. 2000). While deoxygenated aqueous solutions were used for the determination of the products (uranium(IV), aldehyde, and the disappearance of the mercuric ions), measurements of the relative rate of the mercuric ion reduction were carried out in the viscous 10% PVA solution without deoxygenation, as follows. By an addition of aqueous ethanol solution of PVA to a mixture of mercuric chloride and uranyl nitrate, aqueous solutions containing 10% PVA, 20–25% ethanol, 0.005–0.02 *M* mercuric chloride, and 0.005–0.04 *M* uranyl nitrate were prepared in the dark. The viscous solution was placed into an 1-cm depth photometer cell and exposed to light of $\lambda \geq 3650$ Å using a 100-W high-pressure mercury lamp and glass filters (UV-35, UV-39) so that only the uranyl ions absorbed the incident light, the change in the transmittance due to turbidity formation being followed at short intervals during the time of irradiation. The use of the PVA solution had the advantage, besides a practical requirement for preparation of the photosensitive plates, that in such viscous solution the turbidity was

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