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Quenching and Enhancement of Aroyl Luminescence in Excited Nitrogen

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This study investigates both decreases and increases of aromatic carbonyl phosphorescence in excited nitrogen, i.e., in a gas-chromatographic device called the aroyl luminescence detector (ALD). The ALD responds, with nigh specificity, to subpicogram amounts of strongly phosphorescing aroyls. Aroyl response may, however, be quenched by coeluting peaks or gaseous impurities. This deleterious effect has been investigated with O_2, H_2, CH_4, and C_3H_8 as model quenchers. Aroyl phosphorescence is more severely quenched than the nitrogen background, i.e., the so-called second-positive system, N_2 (C $^3\Pi_u$) → N_2 (B $^3\Pi_g$). Oxygen, while being the strongest among the tested quenchers of aroyl phosphorescence, is the weakest quencher of nitrogen emission. The efficiency of various quenchers is similar for aroyl compounds of similar structure. It differs, however—though not by more than a factor of 2—among aroyls of different chemical types. In contrast to these intensity-reducing effects, aroyl phosphorescence is significantly enhanced by the addition of argon to (the carrier and excitation gas) nitrogen. It is proposed that the reaction sequence $Ar^*(^3P_{0,2}) + N_2 \rightarrow N_2(C)^* \rightarrow N_2(B)^* + h\nu \rightarrow N_2(A)^* + h\nu$ results in an increased yield of the metastable N_2(A $^3\Sigma_u^+$) state (this state being considered responsible for the n → π* excitation of aroyl compounds via an efficient triplet−triplet energy-transfer process).

Photochemistry and photophysics of organic molecules have been most widely studied with aromatic carbonyl compounds.[1,2] Luminescence quenching is a very common phenomenon, wherein the nonradiative deactivation of an electronically excited state by a quencher molecule can take place through various mechanisms.[3] The investigation of quenching effects is an important aspect of photochemistry as well as of analytical chemistry: a better understanding of "quenching" is likely to lead to a more comprehensive description of photochemical processes and, in turn, to a more rational design of detection devices and analytical approaches. For obvious reasons, however, luminescence quenching of aromatic carbonyl compounds has usually been studied in condensed phases.[4−9] In contrast, quenching studies in the gas phase are very rare.[10]

A radioactively stimulated, high-voltage (−6 KV), low-current (≤35 nA) discharge in high-purity nitrogen, in the form of the so-called aroyl luminescence detector (ALD) for gas chromatography, can be used to excite certain types of aroyl compounds such as benzaldehyde, benzophenone, and anthraquinone.[11,12] These compounds produce intense gas-phase luminescence (with minimum detectable amounts below 1 picogram) at the otherwise unusual conditions of high temperature and atmospheric pressure.[11,12] The aroyl luminescence is caused by typical triplet → singlet transitions as are characteristic of conventional phosphorescence; however, in this nitrogen discharge, excitation is accomplished by energy transfer not from photons but from metastable dinitrogen molecules.[12,13] This permits the easy study of triplet-state quenching in the gas phase (as opposed to the condensed phases in which phosphorescence is typically observed). For well-understood reasons—such as the absence of solvent effects—the gas phase represents a more fundamental and more interesting system in which to study quenching.

EXPERIMENTAL SECTION

Figure 1 shows the experimental setup. A triple-channel ALD was mounted on a Tracor model 550 gas chromatograph. The construction and operating conditions of the ALD have been described in detail.[12,13] Aroyl-luminescence spectra were acquired by an Oriel model 77250 eighth-meter monochromator equipped with a no. 77298 grating and 0.02−3.2 mm variable slits. The monochromator was operated in the "single-peak" mode. This mode was developed earlier in our laboratory for dual-channel, concentration-referenced, on-line spectral scanning of single GC

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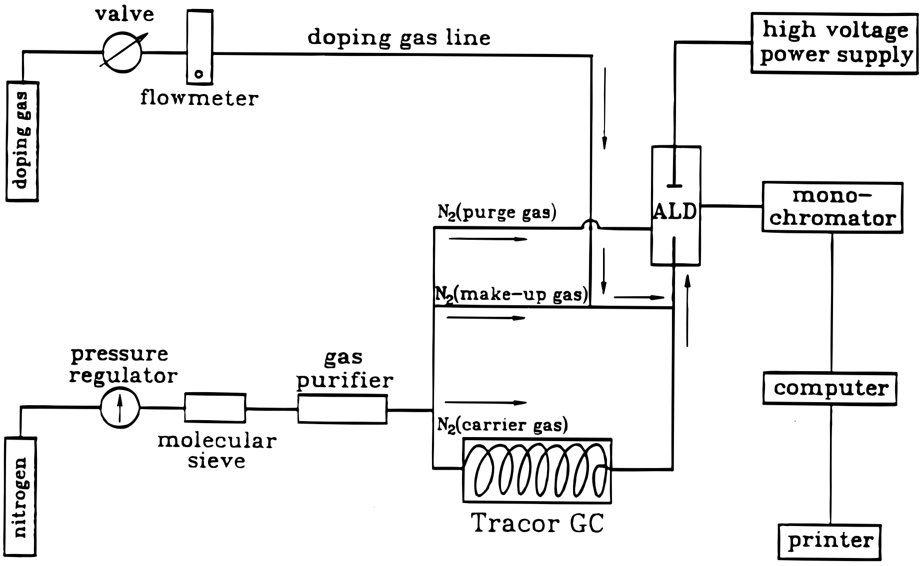

Figure 1. Block diagram of the experimental setup.

peaks.[14] The two channels used for recording spectra were monitored by Hamamatsu R-374 photomultiplier tubes of nominal range 180−850 nm and maximum response at 420 nm. General data manipulation routines have been described elsewhere.[12,15] The wavelength indicator on the monochromator was recalibrated from time to time, using the mercury lines as a standard.

Nitrogen (prepurified, 99.998%), hydrogen (prepurified, 99.99%), and air (extra dry, maximum moisture 10 ppm) were the products of Linde (Linde Union Carbide Canada Ltd., Toronto, ON, Canada). Argon, helium, methane, and propane were ultrahigh-purity gases from Matheson (Matheson Gas Products, Toronto, ON, Canada). All other chemicals (with 95+% purity) came from commercial sources, e.g., from Aldrich Chemical Co. (Milwaukee, WI), Fluka Chemical Corp. (Ronkonkoma, NY), and Sigma Chemical Company (St. Louis, MO). They were used as received for preparing test solutions (usually in acetone).

Luminescence weakening and strengthening experiments were carried out by introducing the quenching or enhancing reagents in gaseous form into the ALD, either through a restricted (i.e., squeezed to near closure) 1/8" copper tube combined with a Nupro fine valve or through a calibrated exponential dilution flask. In the former case, the dopant flow was measured by inserting a bubble flow meter with a low-flow valve into the doping gas line (Figure 1).

RESULTS AND DISCUSSION

Decrease in Luminescence. *Quenching of Nitrogen and Benzaldehyde Emissions.* In an ALD run with pure nitrogen, the "second positive" system of N_2 is the only detectable background emission.[11,12] It is interesting to compare the intensity of quenching by O_2 and CH_4 on both the nitrogen emission and the aroyl phosphorescence. Oxygen and methane play a role in traditional photochemical studies as well as in gas-chromatographic practice; they are used here as model compounds for potentially different quenching modes.

Table 1. Comparison of Quenching of the Nitrogen Second-Positive Emission and the Benzaldehyde Phosphorescence

	concentration (μmol/s) of quencher at 50% quenching of	
quencher	nitrogen second-positive system	benzaldehyde phosphorescence
oxygen	50	0.04
hydrogen	6.8	1.6
methane	50	0.9
propane	2.9	0.4

Table 1 lists the concentration of four quenchers at the point where quenching has reduced the chromatographic peak to 50% of its original size. A direct comparison of the data suggests that benzaldehyde phosphorescence is subject to more severe quenching than the nitrogen second-positive emission. A striking point is that oxygen acts as the strongest quencher of benzaldehyde but the weakest quencher of nitrogen. This difference is clearly portrayed in Figure 2 by the disparate behavior of the two spectra under increasing O_2 loads. That the quenching mechanism of triplet benzaldehyde by triplet oxygen differs from the quenching mechanism of triplet $N_2(C\ ^3\Pi_u)$ is further confirmed by the respective Stern-Volmer plots. In the Stern-Volmer equation

$$I_0/I_p = 1 + k_Q\,\tau\,[Q] \qquad (1)$$

I_0 and I_p are the phosphorescence intensities in the absence and the presence of quencher, respectively, [Q] is the concentration of the quencher, τ is the lifetime of the triplet excited state, and k_Q is the quenching rate constant. The left side of Figure 3 presents the expected and conventional linear plot of $[(I_0/I_p) - 1]$ vs [Q] for benzaldehyde phosphorescence.

However, a similar plot for the quenching of triplet $N_2(C\ ^3\Pi_u)$ did **not** yield a straight line. This is, of course, highly unusual. On spectroscopic grounds it had been suggested[12] that most N_2-(C) molecules in this mild, low-current (<35 nA) discharge

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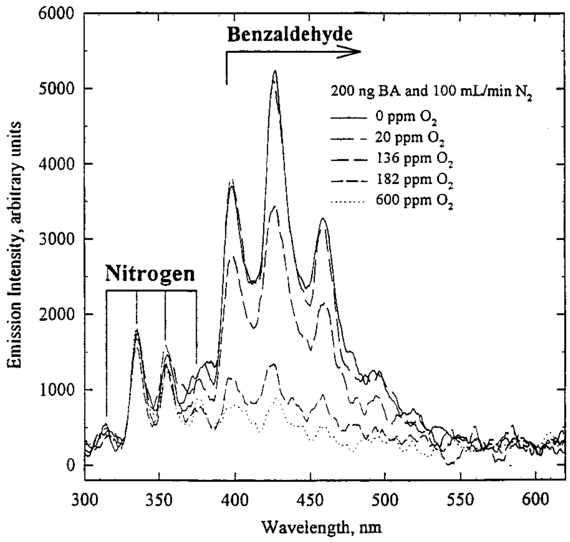

Figure 2. Gas-phase spectra of the nitrogen second-positive system emission and the benzaldehyde phosphorescence, as quenched by oxygen. Spectra were obtained by using a 1/8 m grating monochromator with a R-374 PMT operating in the single-peak mode. Bandpass: 6.6 nm.

originate from a reaction known as "energy pooling":

$$2\,N_2(A\,^3\Sigma_u^+) \rightarrow N_2(X^1\Sigma_g^+) + N_2(C\,^3\Pi_u) \qquad (2)$$

Since this reaction introduces a bimolecular—and likely rate-determining—step into the total quenching sequence, the first-order-based Stern-Volmer equation, eq 1, was adapted to reflect **second**-order kinetics. The corresponding plot of $[(I_0/I_p) - 1]$ vs $[Q]^{1/2}$—as documented on the right side of Figure 3—produces good linearity and hence confirms mechanism (2) for generating the $N_2(C\ ^3\Pi_u)$ state whence the $N_2\ (C\ ^3\Pi_u) \rightarrow N_2\ (B\ ^3\Pi_g)$ background originates.

Table 2. Anthraquinone Response in the ALD at Above-Ambient Pressures

pressure, atm	DC voltage, V	nitrogen background emission, pA	anthraquinone response (4 ng), pA
1.00	5000	551	1108
1.33	6000	572	1240
1.67	7700	555	1337

The different plots of Figure 3 prove that the quenching mechanisms for triplet N_2(C) and triplet benzaldehyde differ from one another. This agrees with the conclusions reached earlier on the basis of relative quenching yields. Unfortunately, the lifetimes of the excited species in the ALD are unknown (and would be difficult if not impossible to determine in this atmospheric-pressure, elevated-temperature environment). This prevents the determination of absolute values for the quenching rate constant k_Q. However, $k_Q\tau$, a constant term reflecting the efficiency of the quencher in deactivating the excited species, can be easily derived from the slope of the lines. As seen in Figure 3, the $k_Q\tau$ values for the quenching of benzaldehyde phosphorescence by oxygen decrease in the order $O_2 > C_3H_8 > CH_4 > H_2$.

Molecular oxygen is a well-known and efficient quencher of fluorescence and phosphorescence in condensed phases,[2,16] where the quenching of the excited states of many organic molecules is diffusion-controlled.[3] In this study, the gas-phase luminescence of aroyl compounds was also quenched by trace amounts of oxygen remaining in the carrier gas or by oxygen diffusing in from the atmosphere. In fact, the use of an oxygen scavenger, i.e., hot zirconium sponge (Supelco), was necessary to keep the oxygen content of the carrier-and-excitation gas nitrogen to its lowest reasonable level. It was also necessary to terminate the exhaust line by an almost closed valve, to maintain the detector at a slight overpressure and minimize the back-diffusion of atmospheric oxygen. Table 2 documents the minor increase of anthraquinone phosphorescence that occurs when the pressure in the detector housing is increased while, for the purpose of

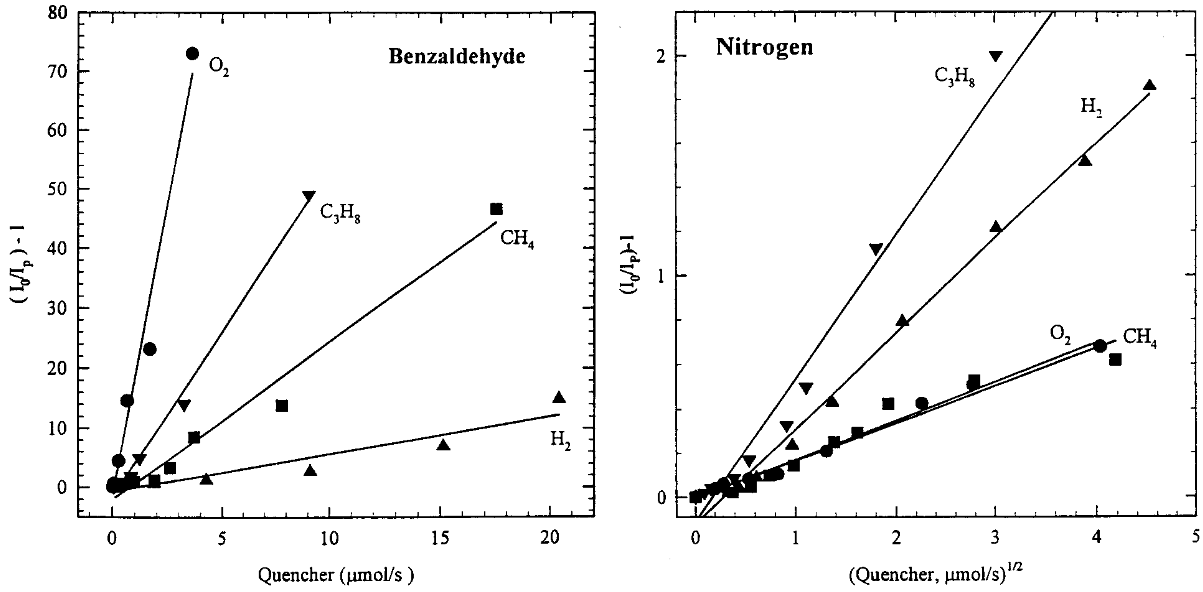

Figure 3. Phosphorescence quenching by oxygen, methane, hydrogen, and propane. Left side: Conventional Stern-Volmer plot for the quenching of benzaldehyde. Right side: Corresponding plot adapted to second-order kinetics, for quenching of the second-positive system of nitrogen.

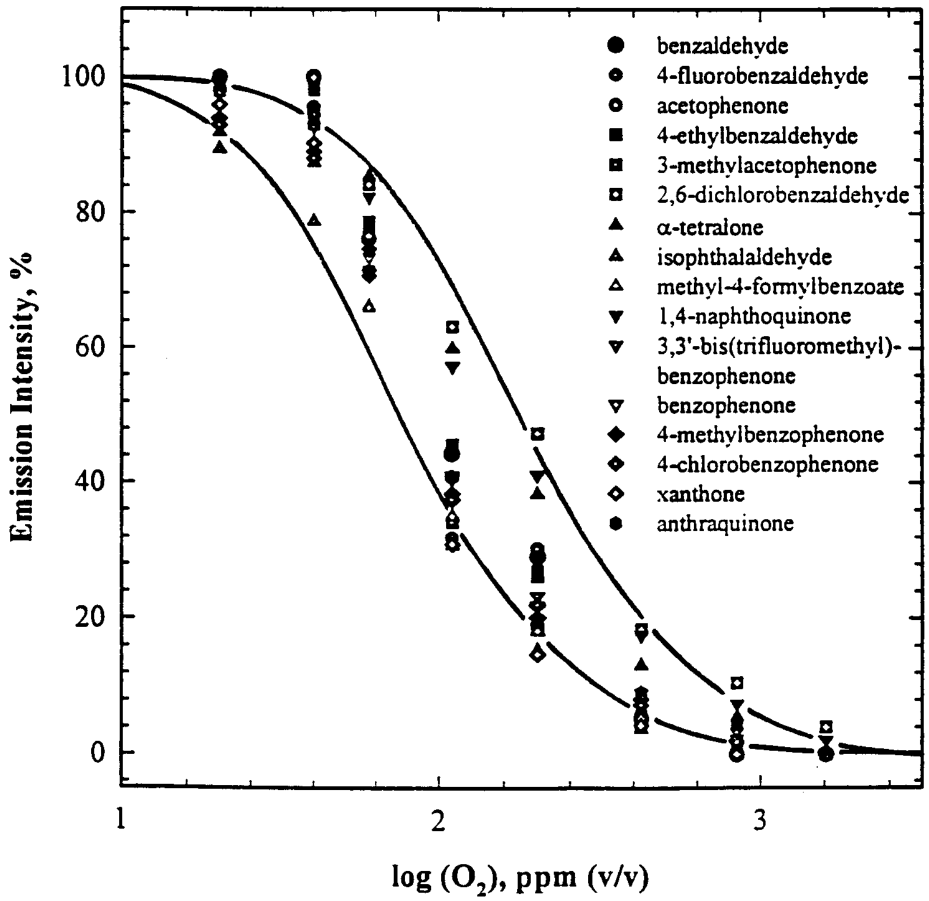

Figure 4. Quenching of sixteen typical aroyl compounds by oxygen. Aroyl compounds in order of elution: 2.5 ng of benzaldehyde, 2.5 ng of 4-fluorobenzaldehyde, 15 ng of acetophenone, 2.5 ng of 4-ethylbenzaldehyde, 10 ng of 3-methylacetophenone, 50 ng of 2,6-dichlorobenzaldehyde, 50 ng of α-tetralone, 2.5 ng of isophthalaldehyde, 2.5 ng of methyl-4-formylbenzoate, 25 ng of 1,4-naphthoquinone, 2 ng of 3,3′-bis-(trifluoromethyl)-benzophenone, 2 ng of benzophenone, 1.5 ng of 4-methyl-benzophenone, 2 ng of 4-chlorobenzophenone, 0.2 ng of xanthone, and 0.35 ng of anthraquinone. For clarity, only the envelope (of strongest and weakest quenching curves) is drawn.

normalization, the nitrogen background emission is kept constant. (The effect is, however, too small to support mechanistic conclusions.)

The precise molecular nature of the reactions between oxygen and the triplet states of the nitrogen carrier and the aroyl analyte are unknown. The literature suggests both chemical and physical processes, e.g., diradicaloid electron transfer or addition and exciplex formation, respectively.[16] On the other hand, given the long radiative lifetime of N_2 ($A\,^3\Sigma_u^+$), this postulated energy carrier for aroyl excitation may also be quenched by collision with an oxygen molecule:[17]

$$N_2(A\,^3\Sigma_u^+) + O_2(^3\Sigma) \rightarrow N_2(X\,^1\Sigma_g^+) + 2O \qquad (\Delta H = -96.4\ \mathrm{kJ/mol}) \quad (3)$$

A significant decrease in the concentration of N_2 ($A\,^3\Sigma_u^+$) would thus clearly lead to a decrease in both the excitation rate of aroyls and, as described earlier, the generation rate of $N_2(C\,^3\Pi_u)$ and, hence, of the N_2 ($C\,^3\Pi_u$) → N_2 ($B\,^3\Pi_g$) background.

General Quenching of Aroyl Luminescence. Figures 4 and 5 show the quenching of 16 typical aroyl compounds by the two premier model quenchers, oxygen and methane. If all compounds and both Figures are considered together, oxygen turns out to be an about 10-fold stronger quencher than methane. More interesting, though, is that the concentration of quencher required to reduce the peak height by half differs by no more than a factor of 2 between the strongest and the weakest quenched aroyl compounds. (Note: Percent quenching depends on the concentration of the quencher, not the quenched.) This suggests that the mechanism for all tested aroyl compounds is structurally similar (and/or that it is mainly controlled by diffusion). However, some correlation is still obtained between quenching intensity and compound structure. While compounds of a similar structure, e.g., the various sustituted benzophenones, are all quenched with similar effectiveness by both oxygen and methane, different-type compounds are quenched to different degrees.

There also appears to exist some correlation between the comparative emission intensity of aroyl compounds and the relative effectiveness of quenchers. This is shown in Figure 6 for 50% quenching by oxygen. (Methane produces a similar picture.) According to these data, stronger emitters are subject to slightly

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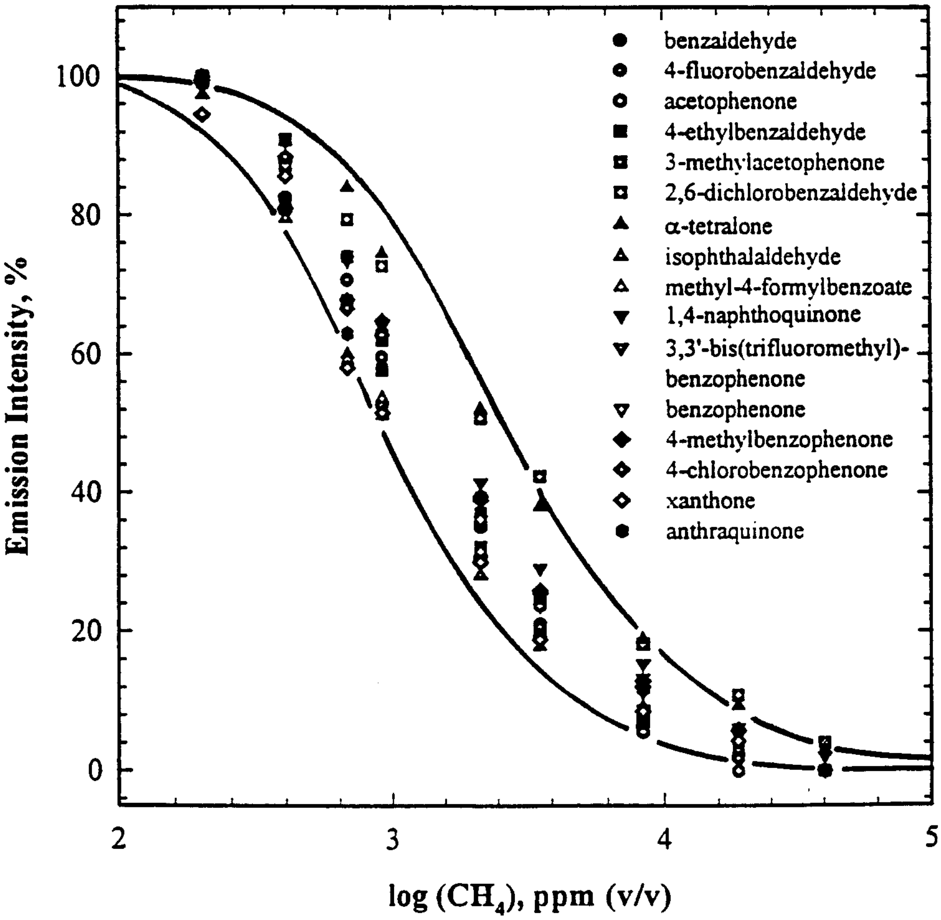

Figure 5. Quenching of sixteen typical aroyl compounds by methane. Aroyl compounds as in Figure 4.

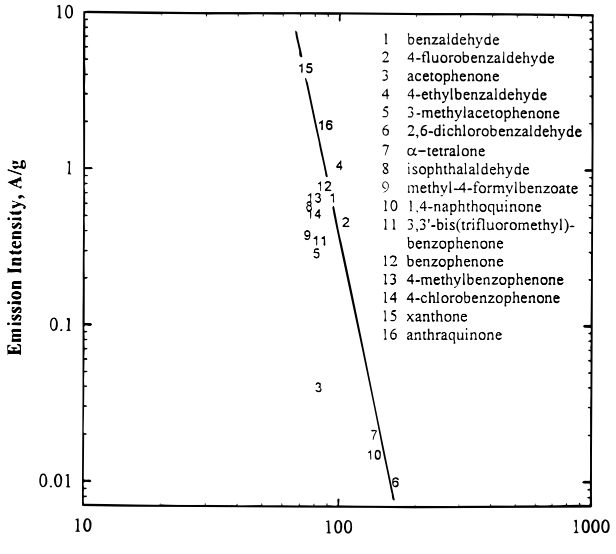

Figure 6. Dependence of oxygen concentration at 50% quenching of aroyl luminescence on the emission intensity of sixteen aroyl compounds.

stronger quenching. The extent of this correlation is, however, close to the experimental error limit.

Analytical Considerations. In this study, analytical quenching processes are modeled by continuously doping the excitation medium with typical or representative quenching gases. This is experimentally convenient and mechanistically appropriate: low levels of oxygen persist in the carrier gas and, more importantly, diffuse in from the atmosphere. Furthermore, the organic compounds that constitute column bleed enter the detector at a more or less constant rate. (Or at a roughly exponential rate in temperature programming.) Such long-term perturbations can be taken into analytical account – as they are indeed in the case of several other gas-chromatographic detectors—by frequent checks of the calibration curve. Nevertheless, the extent of quenching should be kept low and under control by using clean carrier gas and low-bleed columns and by minimizing the back-diffusion of atmospheric oxygen into the system.

Quenching by coeluting peaks is a different matter, however, since such peaks often change from one injected sample to the other, and since a representative sample matrix for each may be difficult to find. For such cases, the method of standard additions works well in the ALD. It has been applied, inter alia, to the analysis of essential oils, harbor sediments, and products of incomplete combustions.[12,18] Graphic examples of quenched ALD responses and ALD/FID chromatograms have been given there and need not be repeated. However, it seems worthwhile to stress that, for processing a complex sample (or a sample where

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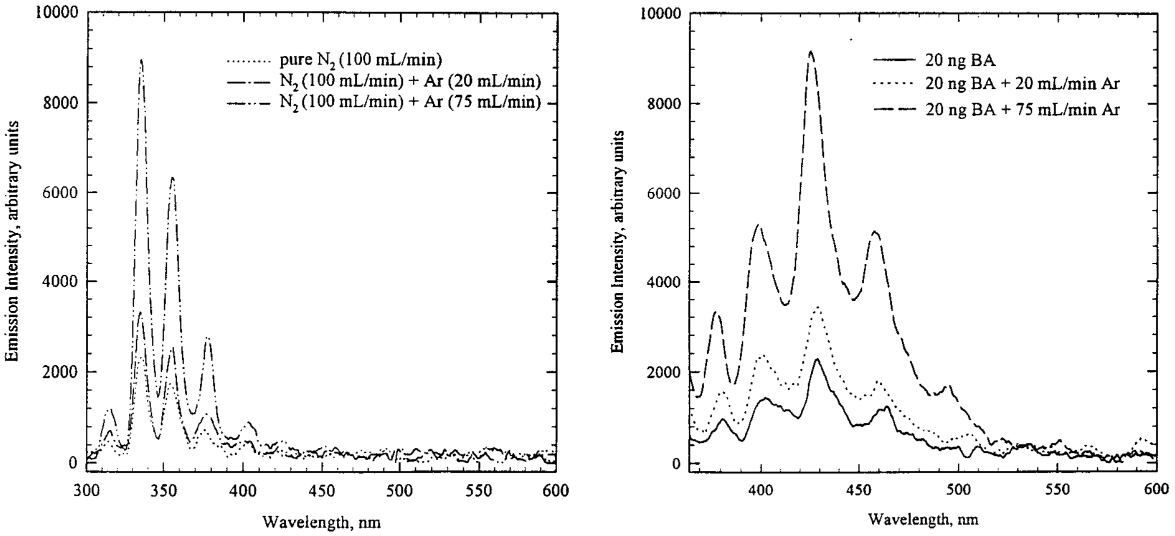

Figure 7. Spectra of the N_2 second-positive emission and of the benzaldehyde (BA) phosphorescence, in pure and argon-doped nitrogen. Eight-meter grating monochromator with R-374 PMT. Band-pass: 6.6 nm.

a second detector, say the FID, alerts the analyst to the presence of larger peaks eluting close to the peak of interest), quantitation should always be checked by the standard-addition technique if a true blank is unavailable.

Increase in Luminescence. *Enhancement of the Nitrogen Second-Positive System and of the Benzaldehyde Phosphorescence.* In excited nitrogen, aroyl compounds are believed to undergo n $\rightarrow \pi^*$ excitation by efficient triplet−triplet energy transfer from the N_2(A) state. Thence they emit phosphorescence (or, in a few cases, E-type delayed fluorescence after intersystem crossing).[12] It was found that the addition of argon to (the carrier and excitation gas) nitrogen strongly enhances the aroyl luminescence as well as the nitrogen background emission. Figure 7 shows the respective gas-phase emission spectra as they increase with the doping level of argon. At the same time, there are no qualitative changes (like wavelength shifts, appearance of new bands, etc.) in the spectra—a fact reassuring to analyst and spectroscopist alike.

An optimization routine was performed on the argon content of the nitrogen carrier. Figure 8 documents the increase in ALD response to both benzaldehyde and nitrogen and the maximum in signal/noise (S/N) ratio of the former. The emission intensity of benzaldehyde clearly and steadily increases with the increase in argon content. (Helium, while showing a similar S/N maximum, behaves less consistently and was therefore rarely used.)

Mechanistic Considerations. Apart from the obvious analytical merit of the argon-doped ALD, the most interesting question is by what mechanism aroyl phosphorescence is actually enhanced in this system. Formally, that is on ground of the gases involved, one might suspect the ALD to be related to the so-called "argon photometric detector" (Ar-PD).[19] The Ar-PD functions similar to Lovelock's well-known and once widely used "argon detector", but it is based on monitoring optical, not electrical, changes. Like the argon detector, the Ar-PD produces argon metastables (at $\sim$11.7 eV) in a mild, radioactively stimulated, pure-argon discharge by electron impact. Any analyte with an ionization potential (IP) below 11.7 eV, such as propane (IP = 11.1 eV) or benzaldehyde (IP = 9.52 eV), is ionized by metastable argon atoms through Penning ionization. The increased electron concentration results in an increased concentration of argon metastables (and of various other species) in the plasma. Therefore, the optical emission of the Ar-PD also increases. Surprisingly, however, this emission consists solely of the nitrogen second-positive system. (Note that nitrogen is always present at trace levels in argon gas and that it diffuses into the GC system from the atmosphere unless stringent precautions are taken.)

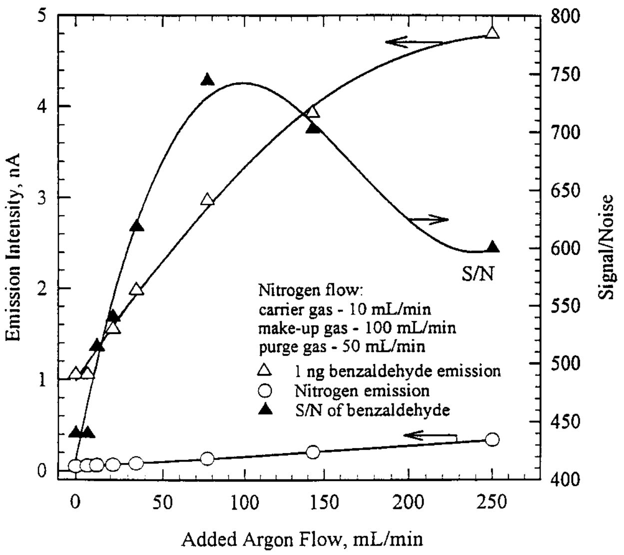

Figure 8. Dependence of benzaldehyde emission intensity, nitrogen second-positive emission intensity, and benzaldehyde signal/noise ratio on added argon flow. The nitrogen second-positive emission was monitored with a 340-nm band-pass filter. DC voltage: 5000 V. PMT (R-268) voltage: −700 V.

In sharp contrast, the ratio of nitrogen to noble gas is much higher in the present argon-doped ALD system (N_2/Ar $\sim$ 1 at the aroyl S/N maximum, as compared to N_2/Ar $\approx 10^{-6}$ in the Ar-PD). When argon is added and benzaldehyde injected into the ALD, there occurs an enhanced emission of benzaldehyde

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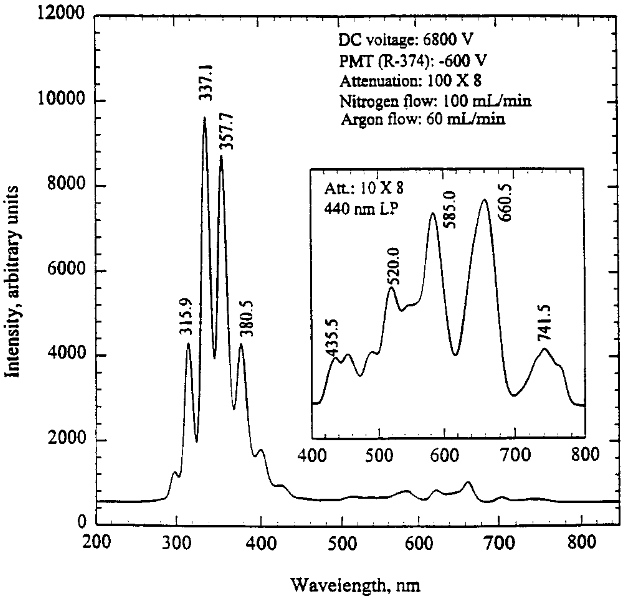

Figure 9. Background spectrum of nitrogen doped with argon in the ALD. Eighth-meter grating monochromator with R-374 PMT. Band-pass: 6.6 nm. A 440-nm long-pass filter was added to suppress the second order in the amplified spectrum.

phosphorescence (aside an enhanced nitrogen second-positive emission), while the electric current remains at about the *same* level. If the energy-transfer mechanism postulated for aroyl excitation is indeed correct, the enhanced aroyl phosphorescence should result from an increased number of triplet metastable $N_2(A)$ states, which are produced by the efficient reaction sequence $Ar^*(^3P_{0,2}) + N_2 \rightarrow N_2(C)^* \rightarrow N_2(B)^* + h\nu \rightarrow N_2(A)^* + h\nu$.[17,20–22] This suggests that aroyl excitation through energy transfer from the $N_2(A)$ state should be the major, if not the predominant, process in the ALD. While it must occur, Penning ionization of analyte—which dominates the Ar-PD—plays only a minor role, if any, in the response mechanism of the argon-doped ALD. (Conversely, aroyl emission is **not** seen in the Ar-PD.) What brings about the increase in emission is the increase in the triplet N_2 (A) species—due, indirectly, to the presence of noble-gas metastables. This suggested mechanism is further supported by the lack of any significant increase in electric current (as occurs very noticeably in the Ar-PD and as constitutes the response of Lovelock's argon detector) when compounds with an IP below 11.7 eV—such as the experimentally used compounds propane, dodecane, acetone or hexane—are injected into the argon- or helium-doped ALD.

Still further evidence for the proposed mechanism is the observation of the very intense second-positive system, as well as of a few, very weak transitions from the first-positive system, $N_2(B) \rightarrow N_2(A)$. Note that the first-positive system occurs mainly in the red/near-infrared region[23] and does not appear to be present in the regular ALD. Figure 9 displays the emission spectra of the intense second-positive plus the weak first-positive system in the argon-doped ALD. (Unfortunately, due to our limited instrumental range of 200 to 800 nm, the main peaks of the first-positive system are beyond observation.) Another bit of supporting evidence is that various band intensity ratios of the nitrogen second-positive system to that of benzaldehyde phosphorescence remain about constant when argon is doped into the nitrogen carrier (Table 3). All this is in agreement with the reaction sequence $Ar^*(^3P_{0,2}) + N_2 \rightarrow N_2(C)^* \rightarrow N_2(B)^* + h\nu \rightarrow N_2(A)^* + h\nu$, with $N_2(A)^*$ being responsible for the additional excitation and similar behavior of both the benzaldehyde phosphorescence and the nitrogen background emission.

Table 3. Nitrogen Second Positive System (N_2) to Benzaldehyde (BA) Phosphorescence Band Intensity Ratios at Different Argon-Addition Rates

ratio of band intensity	argon flow (N_2 flow: 100 mL/min)		
	0 mL/min	20 mL/min	75 mL/min
$I_{337\ \mathrm{nm(N2)}}/I_{427\ \mathrm{nm(BA)}}$	0.91	0.90	0.95
$I_{357\ \mathrm{nm(N2)}}/I_{397\ \mathrm{nm(BA)}}$	1.13	1.03	1.22
$I_{381\ \mathrm{nm(N2)}}/I_{460\ \mathrm{nm(BA)}}$	0.53	0.54	0.50

Analytical Considerations. The improvement in sensitivity conferred upon the ALD by doping it with argon can be used to facilitate the determination of trace amounts of aroyls in complex, real-life samples[18] and enable the acquisition of some weak phosphorescence spectra.[12,13] The extent of this improvement depends on the origin of the baseline noise. As suggested by Figure 8, and as borne out by practical experience, the minimum detectable amount (MDA) for a chromatographic peak in a conventional sample will typically improve by a factor of 2. For measuring spectra, however—where the noise is essentially determined by the dark current of the photomultiplier tube rather than by the background luminescence of the ALD—the improvement increases to more than 4-fold.

CONCLUSIONS

The quenching inflicted by oxygen or hydrocarbons upon the gas-phase phosphorescence of sixteen typical aroyl compounds, and upon the nitrogen second-positive background emission, were investigated in the aroyl luminescence detector (ALD). The quenching data suggested quenching mechanisms that differed for excited aroyl compounds on one hand, and for nitrogen—likely in its triplet $N_2(C)$ state—on the other. Aroyl phosphorescence was quenched strongest, nitrogen emission weakest by molecular oxygen. A minor correlation existed between quenching intensity and compound structure, i.e., compounds of a similar structure were all quenched to essentially the same degree, while compounds of a different structure differed among themselves by a response factor of 2, whether quenched by oxygen or by methane. Unfortunately, the unknown lifetimes of either the triplet $N_2(C)$ state or the excited aroyl compounds did not allow—under the specific conditions of this study—the determination of absolute values for their quenching rate constants, and hence prevented a closer description of the quenching process(es).

In contrast to processes that diminish luminescence, the gas-phase phosphorescence of aroyl compounds in excited nitrogen

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can also be *enhanced*, in this case by doping argon into the carrier-*cum*-excitation gas nitrogen. It is proposed that the enhanced aroyl phosphorescence results from the increased concentration of $N_2(A\ ^3\Sigma_u^+)$ metastables, which are produced by the reaction sequence $Ar^*(^3P_{0,2}) + N_2 \rightarrow N_2(C)^* \rightarrow N_2(B)^* + h\nu \rightarrow N_2(A)^* + h\nu$ and which then serve as energy donors in the excitation of aroyl molecules.

These results are analytically meaningful. While the quenching mechanism(s) call for clean carrier gases and efficient separations when using the ALD (and for use of the standard-additions method should these measures fail to eliminate quenching), the enhancement mechanism(s) offer significant advantages for charting weak phosphorescence spectra and for determining ultratrace amounts of aroyl compounds contained in complex matrixes.

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