

# Sensitized Photolysis and Luminescence of the Tris(ethylenediamine)chromium(III) Ion in Aqueous Solution

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**Abstract:** The energy transfer from biacetyl to  $\text{Cr}(\text{en})_3^{3+}$  has been investigated in aqueous solutions at 15°. The complex quenches the phosphorescent emission of biacetyl but leaves unchanged its fluorescence. Absorption of light by biacetyl leads to  ${}^2E_g \rightarrow {}^4A_{2g}$  phosphorescent emission by the complex (sensitized emission) and also causes the aquation reaction of the complex (sensitized reaction). The quenching of biacetyl phosphorescence by  $\text{Cr}(\text{en})_3^{3+}$ , the intensity of the sensitized emission, and the quantum yield of the sensitized reaction increase with increasing complex concentration and decrease with increasing oxygen concentration. The limit quantum yield of the sensitized reaction ( $\sim 0.8$ ) is noticeably higher than the quantum yield of the direct reaction (0.40). In contrast, the ratio between the limit quantum yield of the sensitized emission and the quantum yield of the direct emission is  $< 1$  ( $\sim 0.6$ ). These apparently contradictory results may be explained assuming that (i) there is a process which quenches the biacetyl triplets and causes the sensitized aquation of  $\text{Cr}(\text{en})_3^{3+}$  without involving electronic energy transfer from biacetyl to  $\text{Cr}(\text{en})_3^{3+}$  or (ii) the excited states of  $\text{Cr}(\text{en})_3^{3+}$  produced by energy transfer are in a more favorable energetic and/or geometrical situation to undergo ligand dissociation than are the excited states produced upon direct excitation.

Electronic energy-transfer processes between organic molecules in solution have extensively been investigated in recent years. The results obtained from these investigations have contributed greatly to the development of organic photochemistry.<sup>1-3</sup> It seems obvious that the extension of such investigations to coordination compounds will prove very useful in order to assess the role played by the various excited states of these compounds in determining their photochemical behavior. Quenching of organic triplet "donors" by coordination compounds had been known for a long time,<sup>4</sup> but the results obtained from such experiments did not permit exclusion of the idea that the quenching was due to a catalytic action of the complex on the radiationless decay of the triplet rather than to a true intermolecular electronic energy transfer. However, Binet, *et al.*,<sup>5</sup> have recently shown that energy transfer is an important factor in the quenching of triplets by Cr(III) complexes in fluid systems at  $-113^\circ$ .

As far as the photosensitized reactions of coordination compounds are concerned, some studies on Co(III) complexes<sup>6-8</sup> and preliminary investigations on  $\text{PtCl}_4^{2-}$ <sup>9</sup> and some Cr(III) complexes<sup>10</sup> have recently been reported.

(1) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1967.

(2) J. C. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966.

(3) A. A. Lamola in "Energy Transfer and Organic Photochemistry," A. A. Lamola and N. J. Turro, Eds., Interscience, New York, N. Y., 1969, p 17.

(4) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, London, 1970, p 29.

(5) D. J. Binet, E. L. Goldberg, and L. S. Forster, *J. Phys. Chem.*, **72**, 3017 (1968).

(6) A. Vogler and A. W. Adamson, *J. Amer. Chem. Soc.*, **90**, 5943 (1968).

(7) G. B. Porter, *ibid.*, **91**, 3980 (1969).

(8) (a) M. A. Scandola, F. Scandola, and V. Carassiti, *Mol. Photochem.*, **1**, 403 (1969); (b) M. A. Scandola and F. Scandola, *J. Amer. Chem. Soc.*, **92**, 7278 (1970).

(9) V. S. Sastri and C. H. Langford, *ibid.*, **91**, 7533 (1969).

Among the Cr(III) complexes,  $\text{Cr}(\text{en})_3^{3+}$  is practically unique in that it shows a luminescent emission in aqueous solution at room temperature,<sup>11</sup> *i.e.*, under the experimental conditions which are customarily used in photochemical investigations. Therefore, this complex would be a very suitable substrate (acceptor) for photosensitization studies, since one can directly verify whether or not electronic energy transfer from the donor to the acceptor really occurs. In this paper, we wish to report the results of a quantitative study on the sensitized photolysis and phosphorescence of  $\text{Cr}(\text{en})_3^{3+}$ , using biacetyl as a donor.

## Experimental Section

**Materials.** Tris(ethylenediamine)chromium(III) chloride dihydrate,  $[\text{Cr}(\text{en})_3]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ , was obtained<sup>12</sup> from its corresponding sulfate salt<sup>13</sup> and then recrystallized three times by addition of  $\text{NH}_4\text{Cl}$ .<sup>12</sup> Biacetyl (2,3-butadienone) "suitable for sensitizer use" was purchased from the Baker Chemical Co. and used without further purification. Deionized distilled water and reagent grade  $\text{HClO}_4$  were also used.

**Apparatus.** Radiations of 401 and 442 nm were isolated from an incandescent lamp by means of Schott and Genossin interference double filters ( $T_{\text{max}}$  42 and 35%, half-width 19 and 13 nm, respectively). For more details concerning the irradiation equipment, see ref 14. The reaction cells were standard spectrophotometric cells (thickness, 1 cm; capacity, 3 ml) housed in a thermostated cell holder. All of the photolysis experiments were carried out at 15°. The incident light was measured by means of the ferric oxalate actinometer,<sup>15</sup> and the light absorbed was calculated on the basis of the transmittance of the solutions. The incident

(10) A. W. Adamson, J. E. Martin, and F. Diomed Camassei, *ibid.*, **91**, 7530 (1969).

(11) W. Geiss and H. L. Schläfer, *Z. Phys. Chem. (Frankfurt am Main)*, **65**, 107 (1969).

(12) M. Linhard and M. Weigel, *Z. Anorg. Allg. Chem.*, **271**, 115 (1953).

(13) C. L. Rollinson and J. C. Bailar, Jr., *Inorg. Syn.*, **2**, 198 (1946).

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(15) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

light was of the order of  $10^{-7}$   $Nh\nu$ /min and the transmittance of the solutions was usually lower than 10%. Spectrophotometric measurements were performed with an Optica CF 4 NI spectrophotometer. The emission spectra were recorded by means of a Turner Spectro 210 spectrofluorimeter. pH measurements were carried out by means of a Knick KpH 350 pH meter.

**Procedures.** The general procedure for the study of the photosensitized photolysis of  $\text{Cr}(\text{en})_3^{3+}$  was as follows. A weighed amount of the complex was dissolved in a solution containing 0.3  $M$  biacetyl and  $\sim 3 \times 10^{-3}$   $M$   $\text{HClO}_4$ . In some of the experiments, the solution was air saturated. In other experiments, the solution was either oxygenated or partially deoxygenated by bubbling with a stream of oxygen or nitrogen, respectively. The bubbling of the appropriate gas was continued after the dissolution of the complex and even during the irradiation, which was carried out in open spectrophotometric cells.

The photoaquation reaction of the complex was followed either by measuring the spectral changes after suitable periods of irradiation with the differential spectrophotometric method (using a non-irradiated solution as a reference) or by measuring pH variations during the irradiation with a glass-reference combined micro-electrode. Because of its sensitivity and accuracy, the latter procedure was a much more convenient one than the former when quantitative data had to be obtained. Moreover, with such a procedure, only a small amount (3–5%) of the complex needed to be decomposed, so that the occurrence of secondary thermal and/or photochemical processes was minimized. Apparent quantum yields for the photosensitized reaction were calculated from the  $\text{H}^+$  vs. absorbed  $Nh\nu$  plots (see Figure 3). When it was necessary, appropriate corrections were made for the light absorbed by the complex and for direct photolysis. No correction was needed for complex absorption of light emitted by biacetyl (the so-called "trivial" sensitization) because of the quenching action of the complex on the biacetyl phosphorescence (see also later discussion).

The procedure used for the study of the direct photolysis was practically the same as above.

As far as the measurements of the direct and photosensitized  $\text{Cr}(\text{en})_3^{3+}$  phosphorescence and the quenching of biacetyl phosphorescence are concerned, care was taken to reduce as far as possible the exposure of the samples to the intense light beam of the spectrofluorimeter, in order to minimize the direct and sensitized photolysis of the complex. Provided that a sufficiently high concentration of  $\text{Cr}(\text{en})_3^{3+}$  was used, the sensitized luminescence was observed for partially deoxygenated, aerated, and oxygenated solutions, which were prepared with the procedure described above. The quenching action of  $\text{Cr}(\text{en})_3^{3+}$  on the biacetyl phosphorescence, on the contrary, could be only observed with solutions which had been accurately deoxygenated (it is well known, in fact, that oxygen has a strong quenching effect on biacetyl phosphorescence<sup>16</sup>). The following complicated procedure had to be used in order to obtain solutions with an oxygen content sufficiently low for allowing a quantitative study of the quenching action of  $\text{Cr}(\text{en})_3^{3+}$ . A biacetyl solution was put into a spectrofluorimeter cell which was connected to a side-arm bulb containing a  $\text{Cr}(\text{en})_3^{3+}$  solution. The arrangement was closed by a thin rubber cover. Both solutions were deoxygenated by bubbling a stream of very pure nitrogen through steel needles for a long time. Then, the spectrofluorimeter cell containing the biacetyl solution was irradiated at 400 nm in order to consume the residual oxygen concentration.<sup>16</sup> The progressive deoxygenation of the solution was followed by the increase in the phosphorescence-to-fluorescence peak ratio.<sup>17</sup> When a satisfactory value of this peak ratio was reached, small amounts of the nitrogen-saturated  $\text{Cr}(\text{en})_3^{3+}$  solution were transferred from the side-arm bulb to the spectrofluorimeter cell by means of a microsyringe whose needle was threaded through the rubber cover of the arrangement.

## Results

**Preliminary Controls.** Before beginning our photochemical and luminescence investigations on acid  $\text{Cr}(\text{en})_3^{3+}$ -biacetyl solutions, we wanted to establish

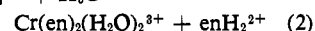
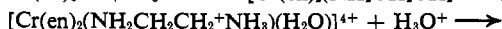
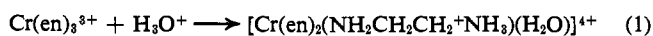
(16) B. Stevens and J. T. Dubois, *J. Chem. Soc.*, 2813 (1962).

(17) It should be noted that the possibility to obtain a low, controlled oxygen concentration (*i.e.*, a reproducible value for the phosphorescence intensity) was very limited. The difficulty in obtaining reproducible phosphorescent intensities has also been pointed out in ref 18.

(18) M. Almgren, *Photochem. Photobiol.*, 6, 829 (1967).

whether disturbing thermal or photochemical reactions occurred in our system.

The thermal behavior of acid  $\text{Cr}(\text{en})_3^{3+}$  solutions was already known from previous investigations.<sup>19</sup> The aquation reaction is a two-step process



The first step (which consists in the rupture of one Cr–N bond, the protonation of the detached ethylenediamine end, and the coordination of a water molecule to Cr) is the rate-determining one. Since this step is very slow at 30°, the thermal aquation of the complex had to be completely negligible in our experimental conditions (15° and time periods shorter than 30 min). In fact, we verified that neither the spectrum nor the pH of a 0.01  $M$   $\text{Cr}(\text{en})_3^{3+}$  solution in  $3 \times 10^{-3}$   $M$   $\text{HClO}_4$  underwent appreciable changes on standing in the dark at 15° for at least 30 min.

The spectrum of a freshly prepared acid solution of biacetyl changed slowly for about 1 hr; afterwards, it remained constant for days. Such a behavior was due to the slow approach to equilibrium between biacetyl and its fairly stable hydrate.<sup>20</sup> For that reason, only aged solutions of biacetyl were used in our investigations.

Upon irradiation in its  $S_1$  band (whose maximum in aqueous solutions is at 406 nm; see Figure 1), biacetyl is known to undergo some photodecomposition reaction which has a quantum yield about  $10^{-2}$  and leads to products which do not absorb in the visible.<sup>21</sup> Accordingly, in the experimental conditions used for the photosensitization experiments (irradiation at 401 nm, light intensity  $\sim 10^{-7}$   $Nh\nu$ /min, irradiation time shorter than 30 min, biacetyl concentration 0.3  $M$ , volume of the irradiated solution 2.5 ml), the loss of biacetyl due to its photodecomposition had to be negligible (about  $1 \times 10^{-5}$  mol/l.). In fact, we found that under the above conditions neither the absorption spectrum nor the pH of a biacetyl solution in  $3 \times 10^{-3}$   $M$   $\text{HClO}_4$  underwent appreciable changes.

Finally, we also verified that neither the absorption spectrum nor the pH of solutions containing 0.3  $M$  biacetyl and  $0.5 \times 10^{-2}$ – $0.2 \times 10^{-1}$   $M$   $\text{Cr}(\text{en})_3^{3+}$  underwent appreciable changes when they were maintained in the dark at 15° for at least 30 min.

**Direct Photolysis of  $\text{Cr}(\text{en})_3^{3+}$ .** According to Geiss and Schläfer,<sup>11</sup> the irradiation of  $\text{Cr}(\text{en})_3^{3+}$  in the wavelength region from 250 to 434 nm (which includes both d–d and charge-transfer absorption bands) causes the occurrence of reaction 1, with quantum yield 0.34–0.38 at 10°. The secondary thermal reaction (2) which follows the photochemical step is negligible at temperatures below 20° and for sufficiently short irradiation periods. Working at pH 3 or lower, reaction 1 may be followed by means of pH measurements.<sup>11</sup> Our experiments were carried out on solutions containing  $10^{-3}$ – $10^{-2}$   $M$   $\text{Cr}(\text{en})_3^{3+}$  and  $\sim 3 \times 10^{-3}$   $M$   $\text{HClO}_4$  (pH  $\sim 2.6$ ), maintained at 15°. The irradiation was performed with 442-nm light, corresponding to the

(19) H. L. Schläfer and O. Kling, *Z. Anorg. Allg. Chem.*, 287, 296 (1956); *Z. Phys. Chem. (Frankfurt am Main)*, 16, 14 (1958); H. L. Schläfer and H. Seidel, *ibid.*, 16, 1 (1958); E. Jørgensen and J. Bjerrum, *Acta Chem. Scand.*, 13, 2075 (1959).

(20) R. P. Bell and A. O. McDougall, *Trans. Faraday Soc.*, 56, 1281 (1960).

(21) J. Lemaire, *J. Phys. Chem.*, 71, 2653 (1967).

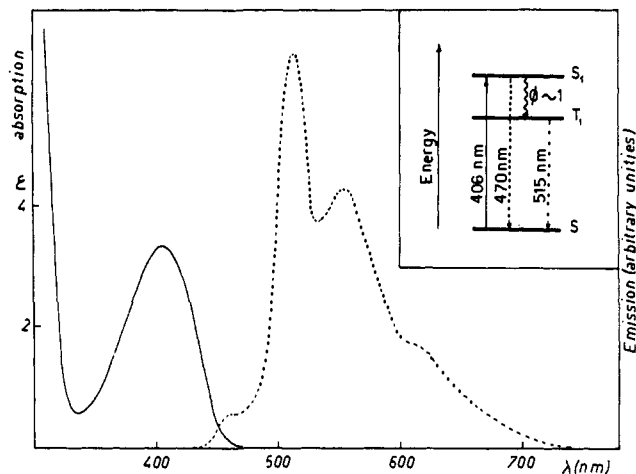


Figure 1. Absorption (—) and emission (---) spectra of biacetyl. The small figure in the square shows the energy levels involved in the transitions.

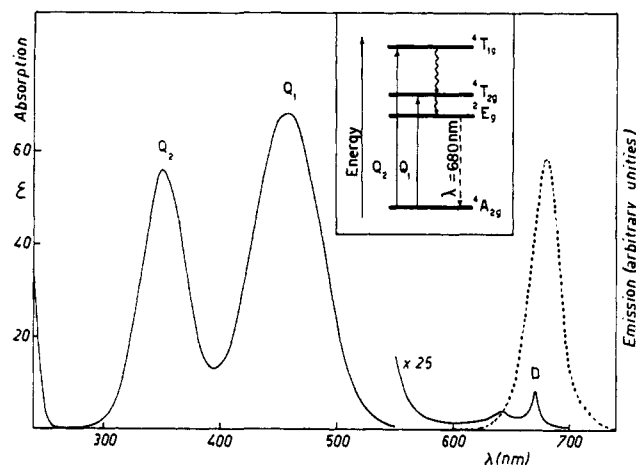


Figure 2. Absorption (—) and emission (---) spectra of  $\text{Cr}(\text{en})_3^{3+}$ . The small figure in the square shows the energy levels involved in the transitions.

lowest spin-allowed d-d band of the spectrum (see Figure 2). The spectral changes obtained upon irradiation were exactly those expected for reaction 1.<sup>19</sup> From the concentration of  $\text{H}^+$  consumed (see Figure 3), the quantum yield of this process was found to be  $0.40 \pm 0.05$ , *i.e.*, in agreement with that found by Geiss and Schläfer<sup>11</sup> using slightly different experimental conditions. We also found that the quantum yield value did not depend on the oxygen concentration of the solutions (see Figure 3).

**Sensitized Photolysis of  $\text{Cr}(\text{en})_3^{3+}$ .** In these experiments, solutions containing  $\sim 0.3 \text{ M}$  biacetyl,  $\sim 5 \times 10^{-3}$ – $2 \times 10^{-2} \text{ M}$   $\text{Cr}(\text{en})_3^{3+}$ , and  $\sim 3 \times 10^{-3} \text{ M}$   $\text{HClO}_4$  were used. When such solutions were irradiated with light of about 400 nm, most of the incident light (from  $\sim 95$  to  $\sim 80\%$ , depending on the complex concentration) was absorbed by biacetyl. Upon irradiation, the absorption spectrum of the solution changed as expected for process 1. Linear plots such as those of Figure 3 were obtained for  $\text{H}^+$  consumed *vs.*  $Nh\nu$  absorbed. After correction for the contribution of direct photolysis,<sup>22</sup> the apparent quantum yield for the sensi-

(22) As mentioned in the Procedures, no correction was needed for complex absorption of the light emitted by biacetyl. In fact, the biacetyl (phosphorescence) emission was completely quenched even when

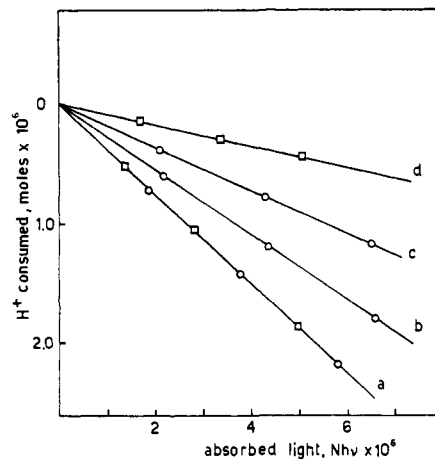


Figure 3. Plots of  $\text{H}^+$  consumed *vs.* absorbed light for solutions containing the following concentrations of complex and biacetyl, respectively: a,  $5.7 \times 10^{-2} \text{ M}$  and 0; b,  $1.0 \times 10^{-2}$  and  $0.3 \text{ M}$ ; c,  $6.5 \times 10^{-3}$  and  $0.3 \text{ M}$ ; d,  $1.0 \times 10^{-2}$  and  $0.3 \text{ M}$ ;  $\circ$ , partially deoxygenated solutions;  $\square$ , oxygenated solutions.

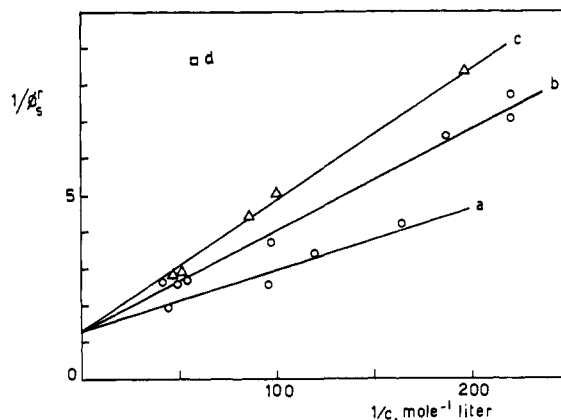


Figure 4. Variation of the quantum yield of the biacetyl-sensitized  $\text{Cr}(\text{en})_3^{3+}$  photolysis with complex concentration: a and b, different stocks of partially deoxygenated solutions; c, aerated solutions; d, oxygenated solution.

tized reaction,  $\phi_s^r$ ,<sup>23</sup> was obtained. The variation of the apparent quantum yield as a function of complex concentration is shown in Figure 4; the limit quantum yield (*i.e.*, the apparent quantum yield for infinite complex concentration),  $\phi_s^r(\text{lim})$ , does not depend on the concentration of dissolved oxygen and is about 0.8.

**Direct and Sensitized Emission of  $\text{Cr}(\text{en})_3^{3+}$ .** When aqueous solutions of  $\text{Cr}(\text{en})_3^{3+}$  were irradiated in the spin-allowed d-d bands, a weak luminescence was obtained. The emission band (Figure 2) is due to the  ${}^2\text{E}_g \rightarrow {}^4\text{A}_{2g}$  transition<sup>24</sup> and has its maximum at about 680 nm (compare with the value  $\sim 670$  nm of the most intense component of the emission at liquid air temperature<sup>25</sup> and with the maximum of the  ${}^4\text{A}_{2g} \rightarrow {}^2\text{E}_g$  transition, which is also shown in Figure 2). We found that the intensity of the emission increased linearly with the lowest complex concentration (whose absorption was  $\sim 10\%$  at 510 nm) was used.

(23) The apparent quantum yield of the photosensitized reaction is the quantum yield for  $\text{Cr}(\text{en})_3^{3+}$  aquation, based on the number of photons absorbed by biacetyl.

(24) Since the arrangement of nitrogen atoms around  $\text{Cr}^{3+}$  is approximately octahedral, the energy levels of  $\text{Cr}(\text{en})_3^{3+}$  are labeled by the Mulliken symbols for  $\text{O}_h$  symmetry.

(25) G. B. Porter and H. L. Schläfer, *Z. Phys. Chem. (Frankfurt am Main)*, **40**, 280 (1964).

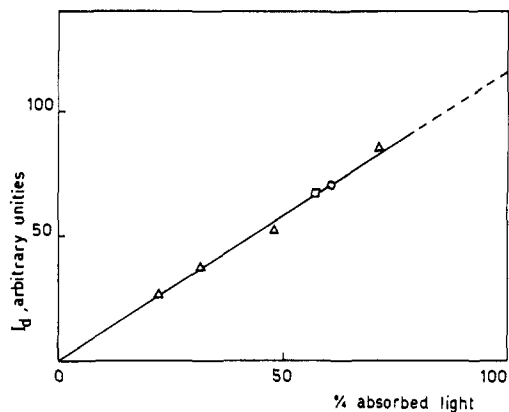


Figure 5. Intensity of the phosphorescence emission of  $\text{Cr}(\text{en})_3^{3+}$  vs. % light absorption:  $\circ$ , partially deoxygenated solution;  $\square$ , oxygenated solution;  $\triangle$ , aerated solutions. The experimental conditions were as follows: excitation at 400 nm; emission at 680 nm; band width of excitation, 15 nm; band width of emission, 25 nm; sensitivity 10.

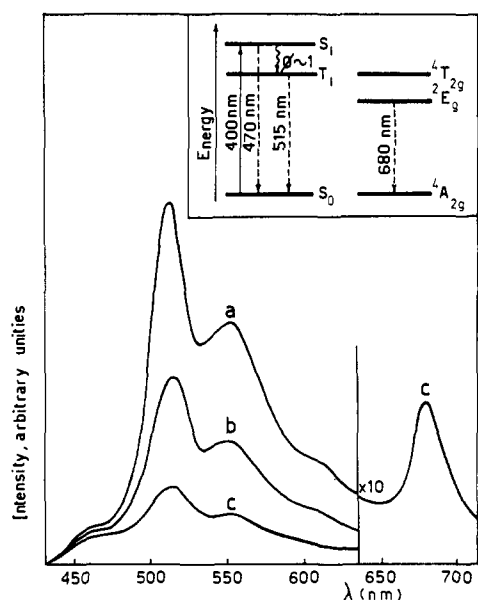


Figure 6. Quenching of the biacetyl phosphorescence by  $\text{Cr}(\text{en})_3^{3+}$  (left side) and biacetyl-sensitized emission of  $\text{Cr}(\text{en})_3^{3+}$  (right side) in partially deoxygenated solutions: a, 0.3 M biacetyl; b, 0.3 M biacetyl and  $1 \times 10^{-3}$  M  $\text{Cr}(\text{en})_3^{3+}$ ; c, 0.3 M biacetyl and  $5 \times 10^{-3}$  M  $\text{Cr}(\text{en})_3^{3+}$ . The small figure in the square shows the energy levels involved in the transitions.

increasing per cent absorption of incident light (Figure 5), and that it did not depend on oxygen concentration.<sup>26</sup>

When deoxygenated solutions of biacetyl were irradiated in the Turner spectrofluorimeter with 400-nm light ( $S_1$  band), a strong emission was observed (Figure 1). As is already known,<sup>27</sup> such an emission consists of a low fluorescence band at about 470 nm and a very intense, structured phosphorescence band with maximum at about 515 nm (the triplet yield for biacetyl is known to be essentially unity in condensed media<sup>27</sup>). In agreement with previous reports, we found that oxygen strongly quenched the phosphorescence, whereas it left

(26) The lack of oxygen quenching on the phosphorescent emission of  $\text{Cr}(\text{en})_3^{3+}$  was also observed by Binet, *et al.*,<sup>6</sup> in fluid solutions at  $-113^\circ$ .

(27) H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, **12**, 823 (1958); **14**, 48 (1960).

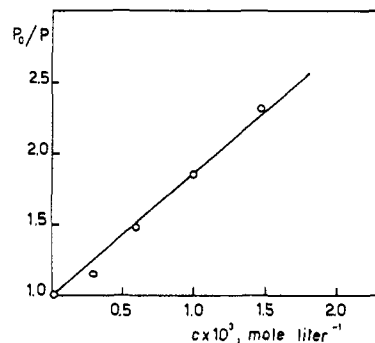


Figure 7. Stern-Volmer plot for the quenching of the biacetyl phosphorescence by  $\text{Cr}(\text{en})_3^{3+}$  (0.3 M biacetyl; accurately deoxygenated solution).

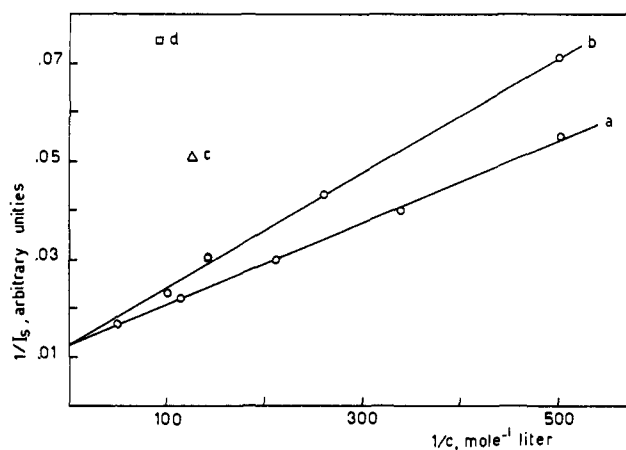


Figure 8. Variation of the intensity of the biacetyl-sensitized  $\text{Cr}(\text{en})_3^{3+}$  phosphorescence with complex concentration: a and b, different stocks of partially deoxygenated solutions; c, aerated solution; d, oxygenated solution; biacetyl concentration, 0.3 M. The other experimental conditions were as indicated in the caption of Figure 5.

unchanged the fluorescence,<sup>27</sup> and that the phosphorescence intensity increased with time of irradiation, due to photochemical consumption of oxygen.<sup>16</sup>

A study of the luminescence spectra of deoxygenated aqueous solutions of biacetyl containing various complex concentrations gave the following results: (i) the biacetyl fluorescence was not quenched by the complex (the small decrease of the emission intensity in the 450–480-nm region, Figure 6, was due to light absorption by the complex); (ii) the biacetyl phosphorescence was strongly quenched (see Figures 6 and 7); (iii) the quenching of the biacetyl phosphorescence was accompanied by the appearance (Figure 6) of an emission band at about 680 nm, which was due to the phosphorescent emission of  $\text{Cr}(\text{en})_3^{3+}$  (compare with the emission band in Figure 2); (iv) after the appropriate corrections for the incomplete light absorption by biacetyl and for the emission due to the absorption of incident light by the complex (3–25%), diagrams such as those of Figure 8 were obtained for the intensity of the sensitized emission as a function of the complex concentration. Note that the intensity of the sensitized emission depended on the oxygen concentration, whereas the limit intensity of emission (*i.e.*, the intensity of emission for infinite complex concentration) was constant.

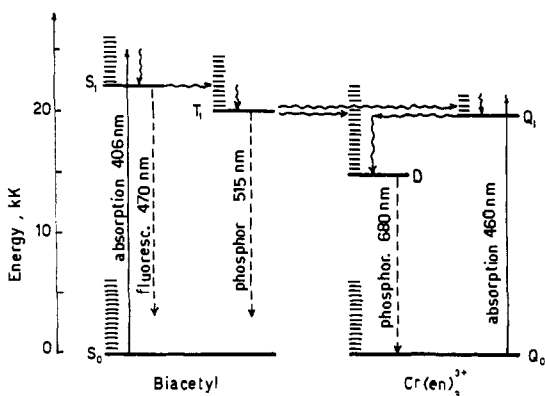


Figure 9. Energy diagram showing the donor (biacetyl) and acceptor ( $\text{Cr}(\text{en})_3^{3+}$ ) levels. Some of the pertinent photophysical processes are also shown.

**Summary of the Experimental Results.** The results obtained with the  $\text{Cr}(\text{en})_3^{3+}$ -biacetyl system may be summarized as follows.

**Solutions Containing Only  $\text{Cr}(\text{en})_3^{3+}$ .** (1) Upon excitation in its  $Q_1$  band,  $\text{Cr}(\text{en})_3^{3+}$  undergoes a photoaquation reaction (process 1), with quantum yield 0.4. (2) Upon excitation in its  $Q_1$  band,  $\text{Cr}(\text{en})_3^{3+}$  emits weakly at about 680 nm ( ${}^2E_g \rightarrow {}^4A_{2g}$  transition; Figure 2). (3) Oxygen does not affect the quantum yield of the photolysis (Figure 3) or the intensity of the phosphorescent emission (Figure 5).

**Solutions Containing  $\text{Cr}(\text{en})_3^{3+}$  and Biacetyl.** (1) The complex quenches the phosphorescence emission of biacetyl (Figure 6), but does not affect the biacetyl fluorescence. (2) Absorption of light by biacetyl ( $S_0 \rightarrow S_1$  transition) leads to light emission by the complex ( ${}^2E_g \rightarrow {}^4A_{2g}$  transition; sensitized emission; Figure 6). (3) Absorption of light by biacetyl ( $S_0 \rightarrow S_1$  transition) causes the photolysis of the complex (sensitized reaction; Figure 3). (4) The intensity of the sensitized emission and the quantum yield of the sensitized reaction increase with increasing complex concentration and decrease with increasing oxygen concentration (see Figures 8 and 4).

## Discussion

**Energy of the Donor and Acceptor Levels.** The electronic states of biacetyl and  $\text{Cr}(\text{en})_3^{3+}$  which play or might play some role in the experiments described above are represented in the energy diagram of Figure 9. Some of the pertinent photophysical processes are also shown in the figure. The energy values of the excited states of biacetyl have been taken from ref 2. The energy value of the doublet state (D) of  $\text{Cr}(\text{en})_3^{3+}$  is obtained from the maximum of the doublet absorption band or from the maximum of the phosphorescent emission (see also ref 25). The energy location of the lowest quartet state ( $Q_1$ ) of the complex is somewhat uncertain. It should be noted, in fact, that this excited state is strongly distorted with respect to the ground state, so that the maximum of its absorption band (*i.e.*, the "vertical" transition from the ground state to the excited state) does not give the difference in electronic energy between the excited state and the ground state, but includes a noticeable amount of vibrational energy of the excited state.<sup>4</sup> From the half-width of the absorption band and from a comparison between the ab-

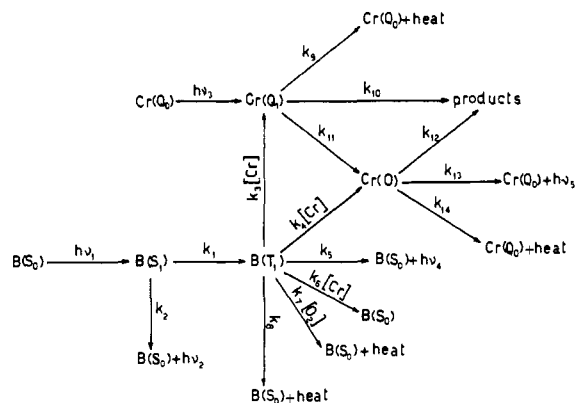
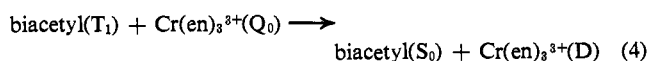
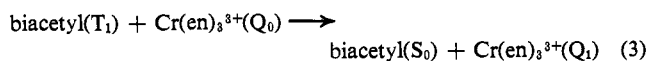


Figure 10. Processes involved in the direct and biacetyl-sensitized photolysis and phosphorescence of  $\text{Cr}(\text{en})_3^{3+}$ .

sorption and fluorescence maxima for the  $\text{Cr}(\text{III})$  complexes which emit fluorescence,<sup>28</sup> it is possible to infer that the zero vibrational level of the  $Q_1$  state of  $\text{Cr}(\text{en})_3^{3+}$  lies at least 2000–3000  $\text{cm}^{-1}$  lower than the energy of the maximum of the absorption band (which is at 21,900  $\text{cm}^{-1}$ ; see Figure 2). This means that  $Q_1$  lies lower than the triplet state of biacetyl; thus, since spin-conservation rules<sup>29</sup> allow transfer from triplet to both quartet and doublet states, the electronic energy transfer from biacetyl to  $\text{Cr}(\text{en})_3^{3+}$  may occur by the following processes



**Kinetic Treatment of the Energy Transfer.** The consecutive and parallel processes which have to be considered in order to account for our experimental results may be summarized as in the scheme of Figure 10. In this scheme, the *direct* emission and photolysis, which start with light absorption by  $\text{Cr}(Q_0)$ , may involve the processes having rate constants  $k_9$ – $k_{14}$ , and the *sensitized* emission and photolysis, which start with light absorption by  $\text{B}(S_0)$ , may involve the processes having rate constants  $k_1$ – $k_{14}$ .

A kinetic treatment based on the scheme of Figure 10 gives the following expressions.

For the quantum yield of the *direct photolysis* of  $\text{Cr}(\text{en})_3^{3+}$  (irradiation in the  $Q_1$  band)

$$\phi_d^r = \frac{k_{10}}{k_9 + k_{10} + k_{11}} + \frac{k_{12}}{k_{12} + k_{13} + k_{14}} \frac{k_{11}}{k_9 + k_{10} + k_{11}} \quad (5)$$

or<sup>30</sup>

$$\phi_d^r = k_{10}\tau_{Q_1} + k_{12}\tau_D\phi_{isc}^{Cr} \quad (6)$$

For the quantum yield of the *direct emission* of  $\text{Cr}(\text{en})_3^{3+}$  (irradiation in the  $Q_1$  band)

(28) H. L. Schläfer, H. Gausmann, and H. Witzke, *J. Chem. Phys.*, **46**, 1423 (1967); H. L. Schläfer, H. Gausmann, and H. U. Zander, *Inorg. Chem.*, **6**, 1528 (1967).

(29) F. Wilkinson, *Advan. Photochem.*, **3**, 241 (1964).

$$\phi_d^e = \frac{k_{13}}{k_{12} + k_{13} + k_{14}} \frac{k_{11}}{k_9 + k_{10} + k_{11}} \quad (7)$$

or<sup>30</sup>

$$\phi_d^e = k_{13}\tau_D\phi_{isc}^{Cr} \quad (8)$$

For the quantum yield of the *biacetyl-sensitized photolysis* of  $\text{Cr}(\text{en})_3^{3+}$  (irradiation in the  $S_1$  band of biacetyl)

$$\phi_s^r = \frac{k_1}{k_1 + k_2} \times \frac{[\text{Cr}]}{k_3[\text{Cr}] + k_4[\text{Cr}] + k_5 + k_6[\text{Cr}] + k_7[\text{O}_2] + k_8} \times \left( \frac{k_3k_{10}}{k_9 + k_{10} + k_{11}} + \frac{k_3k_{11}k_{12}}{(k_9 + k_{10} + k_{11})(k_{12} + k_{13} + k_{14})} + \frac{k_4k_{12}}{k_{12} + k_{13} + k_{14}} \right) \quad (9)$$

or<sup>30</sup>

$$\phi_s^r = \phi_{isc}^B[\text{Cr}]\tau_{T_1}(k_3k_{10}\tau_{Q_1} + k_3k_{11}k_{12}\tau_{Q_1}\tau_D + k_4k_{12}\tau_D) \quad (10)$$

For the quantum yield of the *biacetyl-sensitized emission* of  $\text{Cr}(\text{en})_3^{3+}$  (irradiation in the  $S_1$  band of biacetyl)

$$\phi_s^e = \frac{k_1}{k_1 + k_2} \frac{k_{13}}{k_{12} + k_{13} + k_{14}} \times \frac{[\text{Cr}]}{k_3[\text{Cr}] + k_4[\text{Cr}] + k_5 + k_6[\text{Cr}] + k_7[\text{O}_2] + k_8} \times \left( \frac{k_3k_{11}}{k_9 + k_{10} + k_{11}} + k_4 \right) \quad (11)$$

or<sup>30</sup>

$$\phi_s^e = \phi_{isc}^B[\text{Cr}]k_{13}\tau_D\tau_{T_1}(k_3k_{11}\tau_{Q_1} + k_4) \quad (12)$$

Upon rearrangement, eq 9 and 11 give eq 13 and 14, respectively.

$$\frac{1}{\phi_s^r} = \frac{k_8 + k_4 + k_6}{\phi_{isc}^B(k_3k_{10}\tau_{Q_1} + k_3k_{11}k_{12}\tau_{Q_1}\tau_D + k_4k_{12}\tau_D)} + \frac{1}{\phi_{isc}^B(k_3k_{10}\tau_{Q_1} + k_3k_{11}k_{12}\tau_{Q_1}\tau_D + k_4k_{12}\tau_D)[\text{Cr}]} \quad (13)$$

$$\frac{1}{\phi_s^e} = \frac{k_3 + k_4 + k_6}{\phi_{isc}^B k_{13}\tau_D(k_3k_{11}\tau_{Q_1} + k_4)} + \frac{1}{\phi_{isc}^B k_{13}\tau_D(k_3k_{11}\tau_{Q_1} + k_4)[\text{Cr}]} \quad (14)$$

(30) The following abbreviations have been used

$$\tau_{Q_1} = \frac{1}{k_9 + k_{10} + k_{11}} \quad (\text{lifetime of the } Q_1 \text{ state})$$

$$\tau_D = \frac{1}{k_{12} + k_{13} + k_{14}} \quad (\text{lifetime of the D state})$$

$$\phi_{isc}^{Cr} =$$

$$\frac{k_{11}}{k_9 + k_{10} + k_{11}} \quad (\text{efficiency of the } Q_1 \rightarrow D \text{ intersystem crossing})$$

$$\phi_{isc}^B = \frac{k_1}{k_1 + k_2} \quad (\text{efficiency of the } S_1 \rightarrow T_1 \text{ intersystem crossing})$$

$$\tau_{T_1} = \frac{1}{k_3[\text{Cr}] + k_4[\text{Cr}] + k_5 + k_6[\text{Cr}] + k_7[\text{O}_2] + k_8} \quad (\text{lifetime of the } T_1 \text{ state})$$

It is worth noting that  $1/\phi_s^r$  and  $1/I_s$  ( $I_s$  is the intensity of the sensitized emission, which is proportional to  $\phi_s^e$ ) depend linearly on  $1/[\text{Cr}]$  (see Figures 4 and 8), as expected from eq 13 and 14. It should also be noted that the straight lines obtained for differently oxygenated solutions have, as expected, the same intercept. Finally, note that the value of the Stern-Volmer constant

$$K_s = \frac{k_3 + k_4 + k_6}{k_5 + k_7[\text{O}_2] + k_8} \quad (15)$$

evaluated from the plot of Figure 7, which was obtained by using an accurately deoxygenated solution (see Procedures), is of course much higher than those evaluated from the intercept-to-slope ratio of the plots of Figures 4 and 8, obtained with partially deoxygenated or aerated solutions.

#### Limit Quantum Yield of the Sensitized Reaction.

According to eq 13, the intercept of Figure 4 gives the reciprocal quantum yield of the sensitized reaction,  $\phi_s^r(\text{lim})$ , which represents the quantum yield of the sensitized reaction when  $1/[\text{Cr}] = 0$ , i.e., when all of the biacetyl triplet states are scavenged by  $\text{Cr}(\text{en})_3^{3+}$ . From Figure 4, one can also see that  $\phi_s^r(\text{lim})$  does not depend on  $\text{O}_2$  concentration. It is very important to note that  $\phi_s^r(\text{lim})$  is about 0.8, i.e., much higher than the quantum yield of the direct photolysis ( $\phi_d^r = 0.4$ ); this point will be discussed later.

**Transfer Efficiency.** The limit intensity of the direct emission,  $I_{d(\text{lim})}$ , which may be obtained by extrapolating the data of Figure 5 to 100% absorption, and the limit intensity of the sensitized emission,  $I_{s(\text{lim})}$ , which may be obtained by extrapolating the data of Figure 8 to  $1/[\text{Cr}] = 0$ , are proportional to the quantum yield of the direct emission,  $\phi_d^e$ , and to the limit quantum yield of the sensitized emission,  $\phi_s^e(\text{lim})$ , respectively. Moreover, since the data of Figures 5 and 8 were obtained under the same experimental conditions (see the captions of the two figures), the proportionality constant is the same in both cases. Since  $I_{d(\text{lim})}$  is about 120 (see Figure 5) and  $I_{s(\text{lim})}$  is about 80 (see Figure 8), from eq 8 and 14 one obtains

$$\frac{\phi_s^e(\text{lim})}{\phi_d^e} = \frac{I_{s(\text{lim})}}{I_{d(\text{lim})}} = \frac{\phi_{isc}^B k_{13}\tau_D(k_3\phi_{isc}^{Cr} + k_4)}{k_{13}\tau_D\phi_{isc}^{Cr}(k_3 + k_4 + k_6)} \simeq 0.6 \quad (16)$$

This means that the efficiency of the sensitized emission is lower than the efficiency of the direct emission, contrary to what happens for the efficiencies of the sensitized and direct photolysis (see previous paragraph). Upon simplification, eq 16 reduces to the following one (remember also that  $\phi_{isc}^B$  is practically unity<sup>27</sup>)

$$\frac{k_3 + k_4/\phi_{isc}^{Cr}}{k_3 + k_4 + k_6} \simeq 0.6 \quad (17)$$

It follows that the ratio

$$\gamma = \frac{k_3 + k_4}{k_3 + k_4 + k_6} \quad (18)$$

which expresses the fraction of quenching *via* electronic energy transfer (Figure 10), has an upper limit value (for  $\phi_{isc}^{Cr} = 1$ ) of about 0.6. This means that the quenching of the biacetyl triplets by  $\text{Cr}(\text{en})_3^{3+}$  would occur in part *without* any electronic energy transfer

(process having rate constant  $k_6$  in Figure 10). It should be noted, however, that the above conclusion is based on the assumption that, in eq 16,  $\tau_D$  and  $\phi_{isc}^{Cr}$  in the numerator (where they refer to the sensitized process) have the same values as  $\tau_D$  and  $\phi_{isc}^{Cr}$  in the denominator (where they refer to the direct excitation), so that eq 16 may be reduced to eq 17. This assumption, however, might not be true, as we shall see below.

## Conclusions

The biacetyl- $Cr(en)_3^{3+}$  system is characterized by the following important features: (1) the (limit) quantum yield of the biacetyl-sensitized photolysis of  $Cr(en)_3^{3+}$  is *higher* than the quantum yield of the direct photolysis; (2) the (limit) quantum yield of the biacetyl-sensitized phosphorescence of  $Cr(en)_3^{3+}$  is *lower* than the quantum yield of the direct phosphorescence.

A simple hypothesis which may be used to accommodate these apparently contradictory results is the following one: there exists a path which causes the quenching of biacetyl triplets *and the aquation reaction of  $Cr(en)_3^{3+}$*  without involving electronic energy transfer from biacetyl to  $Cr(en)_3^{3+}$ . Such a path may be that having rate constant  $k_6$  in Figure 10.<sup>31</sup> In fact, biacetyl triplets have long been known to react with molecules containing loosely bound hydrogen atoms, such as amines, alcohols, etc. Thus, it also seems possible that biacetyl abstracts hydrogen from coordinated ethylenediamine, and that this may catalyze in some way the dissociation of the ligand from chromium. This hypothesis, however, does not receive any support from the results obtained with the biacetyl- $Co(NH_3)_6^{3+}$ <sup>3b</sup> and biacetyl- $Co(en)_3^{3+}$ <sup>32</sup> systems, where no sensitized reaction of the complex was observed.

(31) In this case, a term  $k_6$  should be added in the summation found between parentheses in the right-hand side of eq 9. Of course, eq 13 should also be changed.

(32) Unpublished results from our laboratory.

We would like to point out that the apparent contradiction between the photochemical and photophysical results listed above may also be reconciled on the basis of the following speculation. The fate of the excited states  $Q_1$  and  $D$  might depend on the specific position (energy and nuclear coordinates) at which the excited state is *produced* on the potential energy surface. Now, the  $Q_1$  excited state produced by energy transfer may have a different energy than the  $Q_1$  excited state produced by direct irradiation. Moreover, it seems possible that the  $Q_1$  excited state produced by energy transfer, owing to the influence of the donor, may have a distorted nuclear configuration with respect to the ground state  $Q_0$ , whereas distortions cannot occur because of Franck-Condon restrictions when  $Q_1$  is produced by direct excitation. Similarly, the  $D$  excited state produced by energy transfer may have a different energy and nuclear configuration than the  $D$  excited state produced by intersystem crossing from  $Q_1$ . Thus, it might be that the excited states  $Q_1$  and/or  $D$  obtained by energy transfer are in a more favorable situation to give ligand dissociation than they are when produced (directly or indirectly) upon irradiation of the complex.

Stated in other words, while the phosphorescent emission of  $Cr(en)_3^{3+}$  always starts from the lowest vibrational level of  $D$  so that the rate constant of phosphorescence ( $k_{13}$  in Figure 10) does not depend on the "history" through which the  $D$  state is reached, the radiationless deactivations and chemical reactions of  $Q_1$  and  $D$  may start from high vibrational levels, and thus the actual values of the rate constants  $k_9$ ,  $k_{10}$ ,  $k_{11}$ ,  $k_{12}$ , and  $k_{14}$  in Figure 10 may depend on the way in which the excited state is produced. This would also imply that, as previously mentioned, eq 16 cannot be simplified into eq 17, so that the upper limit value ( $\sim 0.6$ ) estimated above for the transfer efficiency might be meaningless.

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