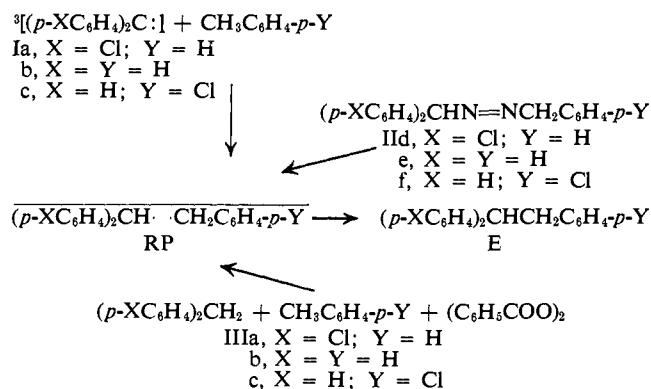


Table I. Mixing Coefficients, M_j , for AB_2 Systems^a

| j | M_j |
|--|--|
| $\beta\beta\beta$ | $\beta H_0 \Delta g / 2 - A_1 / 4 + A_2 / 2$ |
| $\alpha\beta\beta$ | $\beta H_0 \Delta g / 2 + A_1 / 4 + A_2 / 2$ |
| $2^{-1/2} \beta(\alpha\beta + \beta\alpha)$ | $\beta H_0 \Delta g / 2 - A_1 / 4$ |
| $2^{-1/2} \beta(\alpha\beta - \beta\alpha)$ | $\beta H_0 \Delta g / 2 - A_1 / 4$ |
| $2^{-1/2} \alpha(\alpha\beta + \beta\alpha)$ | $\beta H_0 \Delta g / 2 + A_1 / 4$ |
| $2^{-1/2} \alpha(\alpha\beta - \beta\alpha)$ | $\beta H_0 \Delta g / 2 + A_1 / 4$ |
| $\beta\alpha\alpha$ | $\beta H_0 \Delta g / 2 - A_1 / 4 - A_2 / 2$ |
| $\alpha\alpha\alpha$ | $\beta H_0 \Delta g / 2 + A_1 / 4 - A_2 / 2$ |

^a Nuclear spin characterized by hyperfine constant A_1 is on component 1. The two identical spins characterized by A_2 are on component 2; $\Delta g = g_1 - g_2$.

$w_{er} > 50w_j$; Δg was adjusted to fit the experimental results, giving the values 8×10^{-4} , 1.6×10^{-4} , and -5×10^{-4} for spectra a-c, respectively. There is good semiquantitative agreement, and the g -shift differences are within expectations.⁷



The theory predicts (eq 9 of ref 3) that singlet-derived E from reaction II should show spectra with opposite polarizations. Figure 1 (spectra d-f) shows the experimental results from reactions II d-f and the calculated relative intensities of the transitions using the same parameters used for reaction I. Again agreement is acceptable. Variation of Δg from positive to negative values shifts the signals of the methine protons from net emission to net absorption, and those of the methylene protons go from absorption to emission. The trend is reversed in the singlet reaction. With $\Delta g = 0$, each group of proton signals shows a multiplet with no net polarization.

The spectra arising from reaction III can be understood if one assumes the following model. The individually generated benzhydryl and benzyl radicals form on collision new radical pairs with spins in random phase. This corresponds to half-singlet and half-triplet character (not including $|1,1\rangle$ and $|1,\bar{1}\rangle$ states). The time development of this state results from the loss of RP to coupling product which in turn leads to an increase in the triplet character in the remainder. This provides the basis for triplet-singlet mixing *via* the hyperfine and g -shift mechanism. Therefore the type of polarization expected is that observed in the triplet reaction I, only of smaller magnitude. In agreement with this prediction all spectra derived from reactions III a-c had identical relative intensities as those obtained from reactions I a-c which are shown in Figure 1 a-c.

(7) The calculated relative intensities should be regarded as demonstrative rather than as best fits, because A_1 and A_2 cannot be expected to be constant in all three reactions. Also, for an exact fit the phenyl protons would have to be included.

Finally, it is worth noting that the model assumes a lifetime of the free radicals longer than T_1 of the nuclei in free radicals (10^{-4} - 10^{-5} sec). This assumption is most probably correct for cases where radical coupling and disproportionation reactions are the only pathways available. If, however, the radicals are more reactive than benzylic radicals, other reactions, such as transfer reactions to the solvent or other substrates, are possible, and the final diamagnetic compound may show nuclear spin polarizations originating from free radicals which escaped the cage by diffusion. We will discuss these cases in future publications.

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Vapor-Phase Photolysis of Phenyl Acetate

Sir:

The photo-Fries rearrangement, the photochemical conversion of phenyl esters to *o*- and *p*-hydroxyphenones, has been investigated extensively in solution and shown to give varying amounts of phenol in addition to the two major photoproducts.¹⁻¹² As an example, phenyl acetate rearranges in cyclohexane to give *o*-hydroxyacetophenone $\phi = 0.17$, *p*-hydroxyacetophenone $\phi = 0.15$, and phenol $\phi = 0.06$.⁷ Mechanistic studies of this rearrangement in solution do not distinguish clearly between two pathways to the hydroxyacetophenones. In one mechanism, a solvent cage recombination of the acyl and phenoxy radicals gives the observed photoproducts,^{3,7} and in the other the *o*- and *p*-hydroxyphenones are formed *via* a concerted mechanism in which the phenoxy and acyl portions of the molecule remain bonded throughout the rearrangement.^{2,5,6,8} While the first mechanism neatly accounts for the formation of phenol by simple escape of the phenoxy radical from the solvent cage followed by hydrogen abstraction from the solvent, the concerted mechanism requires that the phenol be produced by a separate, competing photoreaction of the phenyl acetate. Although we have no deep-seated prejudice against dual pathways in the chemical decay of excited states, there is a real problem in that approach in this case. If radical pairs are produced, common experience indicates that some should undergo geminate recombination including coupling at the *ortho* and *para* positions of the aromatic ring. While most of the attempts to reach mechanistic conclusions have been obtained from sol-

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vent-viscosity and solvent-polarity studies on the quantum yields for each of the photoproducts, it seemed advantageous to us to remove the solvent altogether. Irradiation of phenyl esters in the vapor phase eliminates the possibility of formation of the *o*- and *p*-hydroxyphenones by the cage recombination pathways and provides a test of the concerted reaction mechanism proposed for the photo-Fries rearrangement. For this reason we wish to report some preliminary results from our studies of the vapor-phase photolysis of phenyl acetate. To our knowledge this is the first report of the irradiation of a phenyl ester in the vapor phase.

Preliminary experiments in static systems gave at least 25 product peaks when analyzed by gas-liquid partition chromatography (glpc), so we turned to a flow system. The flow system consisted of a heated quartz tube (50°) through which a nitrogen-isobutane gas mixture carried vaporized phenyl acetate past a battery of 2537-Å lamps.^{13,14} The isobutane was added to provide a source of hydrogen atoms for radical abstraction processes. The photoproducts and unreacted phenyl acetate were collected at -78°. With the carrier gas flow adjusted to give a residence time of 55 sec in the irradiation tube, phenyl acetate conversions of about 4-5% were obtained. Analysis of the product mixture by glpc revealed six products in appreciable amounts, of which the major peak made up 65% of the total photoproducts (by peak area).¹⁵ Of the remaining five products, two were present in about 10% yield and three in about 5% yield. The major peak comprising 65% of the products was identified as phenol by glpc. The identity was established by comparison of chromatograms of the reaction mixture with those containing reaction mixture plus an authentic sample of phenol. Increased peak height without change in peak shape on three different glpc columns was taken as proof of the presence of phenol in the photoproduct mixture.¹⁶ Although the identity of the remaining five photoproducts has not as yet been established, it is clear from results of the same glpc identification technique applied to the *o*- and *p*-hydroxyacetophenones that neither of these two compounds, formed in high yield in solution, are among the major products of the vapor-phase irradiation of phenyl acetate.^{17,18} Likewise, glpc analysis showed less than 1% of anisole and toluene.

In addition to these photoproducts, a considerable

(13) A more detailed description of the flow system apparatus will appear later in a full paper.

(14) Three PCQ-X1 low-pressure mercury vapor lamps, manufactured by Ultraviolet Products Inc., San Gabriel, Calif., provided an unusually intense, pure source of 2537-Å light.

(15) Glpc analysis was accomplished on a Hewlett-Packard 5750 temperature-programming gas chromatograph with flame ionization detection. A 7 ft × 1/8 in. column of 10% DC-LSX-3-0295, a trifluoropropylmethyl and vinyl copolymer, on 60-80 Chromosorb W (acid washed) was used to separate the components of the photoproduct mixture.

(16) Glpc columns used to establish the presence of phenol in the photoproduct mixture were: (1) 7 ft × 1/8 in. 10% DC-LSX-3-0295 on Chromosorb W (acid washed); (2) 5 ft × 1/8 in. 5% SE-30 on Chromosorb W (acid washed, DMCS); (3) 5 ft × 1/8 in. 5% XE-60 on Chromosorb G (acid washed, DMCS). Phenol had a relative retention time shorter than phenyl acetate on both the LSX and SE-30 columns, while the opposite was true with the XE-60 column; *i.e.*, phenyl acetate was eluted before phenol.

(17) Authentic samples failed to enhance any of the glpc peaks of the product mixture when chromatographed on the LSX column.

(18) The stability of the *o*- and *p*-hydroxyacetophenones was established by earlier experiments in static systems. In addition, *o*-hydroxyacetophenone has been irradiated in the flow system under conditions identical with those of the phenyl acetate irradiations and gave no traces of the photoproducts observed in this work.

amount of brown solid was formed which proved to be insoluble in the usual organic solvents but was soluble in 10% aqueous potassium hydroxide. This latter fact suggests that the intractable brown solid might be a phenolic polymer. However, this has, as yet, not been established, and work is continuing on this aspect of the problem.

Results of this study suggest that since no *o*- or *p*-hydroxyacetophenone was found among the six photoproducts, a concerted mechanism cannot be important in the vapor-phase irradiations of phenyl acetate.¹⁹

The absence of significant amounts of toluene suggests that the concerted decarboxylation side reaction reported to take place in nonpolar solvents by Finnegan and Knutson^{10,12} is apparently not operative in the gas phase.

Similarly, decarbonylation to give anisole is not observed. However, this reaction, which is important in the solution photochemistry of some phenyl esters, is postulated to proceed through a radical solvent cage recombination mechanism,^{10,12} and obviously there is no cage to constrain the radicals in the gas phase.

Thus, both the high yield of phenol and failure to produce appreciable amounts of either anisole or *o*- or *p*-hydroxyacetophenone are consistent with a mechanism in which the primary step involves fragmentation of an excited phenyl acetate molecule to acyl and phenoxy radicals. These two radical fragments diffuse apart in the vapor phase, and the phenoxy radical eventually abstracts hydrogen from isobutane to form phenol, while the acyl radical probably undergoes decarbonylation^{6,20} or is involved in polymerization.³ Although we cannot exclude the possibility of the appearance of an additional mechanism in the solution, we do not believe such a view is necessary to explain the known solution photochemistry of phenyl acetate. Inclusion of a solvent cage recombination step is all that is required to produce a mechanistic pathway by which acyl and phenoxy radicals can recombine to give *o*- and *p*-hydroxyacetophenone, the major products of the photo-Fries rearrangement. A similar mechanism has recently been proposed to explain the solution and vapor-phase photochemistry of acetanilide.^{21,22}

Work is continuing to determine the identities of the other five major photoproducts of this reaction and their relationships to the mechanism of the photo-Fries rearrangement.

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(19) A referee has suggested that acetylcyclohexadienones, the presumed precursors of the products of the photo-Fries rearrangement in solution, may be formed by a concerted process in the gas phase and subsequently photolyzed yielding the observed products. We doubt if this interesting hypothesis can be correct because rapid intramolecular enolization of 2-acetyl-3,5-cyclohexadienone to give *o*-hydroxyacetophenone would be expected to be quite fast. Since *o*-hydroxyacetophenone is not among the major photoproducts (despite its stability under the conditions), one is drawn to the conclusion that the biphotonic process is an unlikely mechanism for the gas-phase reaction.

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Lifetime of the ${}^4T_{2g}$ State of Chromium(III) Complexes

Sir:

Primary photoprocesses of chromium(III) complex ions in their lowest doublet state, 2E_g , have been followed through the phosphorescent emission: ${}^2E_g \rightarrow {}^4A_{2g}$.¹⁻³ However, except for a few complexes from which fluorescence can be measured, the lowest excited quartet, state ${}^4T_{2g}$, cannot be similarly studied. Fluorescence is not usually observed if the state 2E_g lies appreciably lower in energy than ${}^4T_{2g}$, which is the case for large ligand-field splittings.⁴ Delayed fluorescence can also be observed at high temperatures,³ but fluorescence must always occur; it may go undetected in steady-state experiments because of its continuous broad spectrum and low intensity, as is the case with fluorescence from the lowest singlet excited state of azulene.⁵ The important question of what excited state is directly involved in the photoaquation of chromium(III) complex ions^{6,7} cannot be answered until more is known about their properties. We present data here on the lifetimes of the 2E_g and ${}^4T_{2g}$ states for chromium complexes with various ligands. We also report, from a crude spectrum of the fluorescence of the hexacyanochromate(III) ion, an unexpectedly large Stokes' shift between absorption and emission.

The apparatus used consisted of a condensed flash lamp dissipating about 5 J with a half-width of *ca.* 200 nsec, isolated optically from a monochromator-detector system by complementary filters. At the sensitivities used, no scattered exciting light could be detected. The detector, a Philips 150CVP (S-1 response) photomultiplier, was attached to the exit slit of a Bausch & Lomb monochromator used with a band width of 22 nm. The output of the multiplier was in turn fed into a Tektronix 543B oscilloscope. The time constant of the detector was adjusted, by a capacitor across the load resistor, so as to be less than that of the lifetime studied by a factor of 100. All measurements were made with clear rigid glass solutions at 77°K (either 2:1:1 methanol:water:ethylene glycol or 1:1 methanol:ethanol, depending on solubility). Excitation was into the quartet state manifold of the complexes and the luminescence was generally studied at the known phosphorescence maxima.^{8,9}

The luminescence decay curves, when examined at

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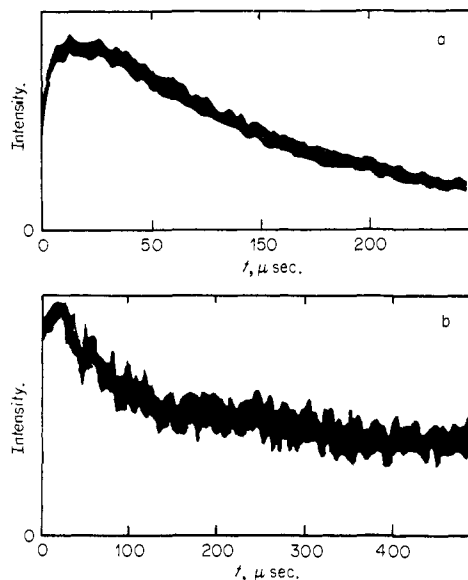


Figure 1. Oscilloscope traces of luminescence decay: (a) $\text{Cr}(\text{acac})_3$, (b) $\text{Cr}(\text{CN})_6^{3-}$.

slow oscilloscope sweep speeds (*ca.* 0.5 msec/div), show the normal exponential phosphorescence decay. The lifetimes, τ_p , shown in Table I are in good agreement with those of Chatterjee and Forster.⁹ At higher sweep speeds (up to 1 $\mu\text{sec}/\text{div}$) there is an increase in intensity during the first 50 μsec (see Figure 1a) to a maximum followed by the relatively slow phosphorescence decay. We associate this increase with population of the phosphorescent state *via* intersystem crossing. The lifetime τ_f associated with this initial rise, found by fitting the data to the equation

$$I = A\{e^{-t/\tau_p} + \alpha e^{-t/\tau_f}\} \quad (1)$$

thus represents the lifetime of the lowest excited quartet state, ${}^4T_{2g}$. The constant α , as will be shown, would have the value -1 if only phosphorescence is observed and a value greater than -1 if both fluorescence and phosphorescence are detected. The data are collected in Table I.

Table I. Reciprocal Lifetimes and Rate Constants (sec^{-1}) in the Luminescence Decay of Chromium(III) Complexes

| Complex | $(1/\tau_p)$ $\times 10^{-3}$ | $(1/\tau_f)$ $\times 10^{-4}$ | k_2 (calcd) $\times 10^{-4}$ | α |
|----------------------------------|----------------------------------|----------------------------------|-----------------------------------|-------------------|
| $[\text{Cr}(\text{NCS})_6]^{3-}$ | 0.23 | 12 | 80 | -0.47 |
| $[\text{Cr}(\text{CN})_6]^{3-}$ | 0.29 | 2.0 | 19 | +1.6 ^a |
| $[\text{Cr}(\text{acac})_3]$ | 2.8 | 12 | 36 | -0.40 |
| Reineckate ion | 3.0 | 13 | 72 | -0.38 |
| $[\text{Cr}(\text{tn})_3]^{3+}$ | 9.3 | 13 | | -0.47 |
| $[\text{Cr}(\text{en})_3]^{3+}$ | 10.0 | 8.9 | 70 | -0.38 |

^a At 830 nm. Value of α depends on the wavelength monitored.

We assume in the following treatment that the luminescence measured in the decay curves is both fluorescence and phosphorescence. The simple mechanism of DeArmond and Forster¹⁰ gives the following expressions for the intensity of fluorescence and of phosphorescence at any one wavelength as a function

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