whether HF has any significant effect on the reaction. At the temperatures used, a significant amount of F_2 and Xe is in equilibrium with XeF_2. Thus elemental fluorine, as well as XeF_2, is available to initate reaction. Once phenyl radicals are formed, a sequence such as

$$C_6H_5\cdot + XeF_2 \longrightarrow C_6H_5F + XeF\cdot$$
$$XeF\cdot + C_6H_6 \longrightarrow C_6H_5\cdot + HF + Xe$$

would be expected to operate. With nitrobenzene, meta orientation by the NO_2 group is observed as expected. In the case of a fluorine atom on the ring, para orientation is favored and there appears to be as much of an inhibiting effect for ortho as for meta substitution.

It is concluded that vapor-phase reaction with XeF_2 leads to facile, easily controlled substitution of aromatic compounds. The method appears to be general and may offer some advantages in ease of handling over reaction in solution. The main limitation is the low volatility of the higher aromatics, and for these substances reaction in inert solvent will be preferable. However, vapor phase reaction will still be feasible for compounds like naphthalene and biphenyl at temperatures below 200°.[6]

Acknowledgment. We are indebted to Mr. R. Smol for expert technical assistance.

[6] For example, the vapor pressure of biphenyl is 100 mm at 180° and that of naphthalene is nearly 300 mm. Nitrobenzene (bp 211°) was successfully substituted at 120° where its vapor pressure is only 50 mm.

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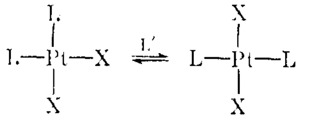
Received May 20, 1970

Ligand–Complex Interaction in Tetragonal Planar Complexes and the Mechanism of Catalyzed Isomerization[1]

Sir:

Associative interactions appear to be very important in the chemistry of tetragonal planar complexes.[2] Both substitution reactions and homogeneous catalysis can be understood in terms of associative mechanisms. Through study of isomerization of platinum(II) complexes (eq 1), we have obtained considerable insight into the nature of association in tetragonal planar complexes. The results are also of importance to the problem of fluxional changes in structure of coordination compounds.



$$\mathrm{L{-}\overset{L}{\underset{X}{Pt}}{-}X \;\overset{L'}{\rightleftharpoons}\; L{-}\overset{X}{\underset{X}{Pt}}{-}L} \qquad (1)$$

1 2

When *cis*-bis(trialkylphosphine)dichloroplatinum(II) (**1**: X = Cl, L = R_3P) complexes are mixed in cyclohexane with a catalytic amount of phosphine (L′), the rate of isomerization can be measured spectrophotometrically.[3] When L′ = L or L′ ≠ L, well-behaved, first-order rates are observed and each system has an unique second-order rate constant evaluated from first-order rate constants over a range of [L′]. For example, at 30°, when $L = L' = (n\text{-}C_3H_7)_3P$, $k_2 = 2.60 \times 10^2\ M^{-1}\ sec^{-1}$, but when $L = (n\text{-}C_3H_7)_3P$ and $L' = (n\text{-}C_4H_9)_3P$, $k_2 = 4.50 \times 10^2\ M^{-1}\ sec^{-1}$. Or, when $L = L' = (n\text{-}C_4H_9)_3P$, $k_2 = 4.50 \times 10^2\ M^{-1}\ sec^{-1}$, but when $L = (n\text{-}C_4H_9)_3P$ and $L' = n\text{-}C_4H_9P(C_6H_5)_2$, $k_2 = 1.84 \times 10^2\ M^{-1}\ sec^{-1}$.[4] Since the total amount of L is greater by at least a factor of 20 than L′, exchange of L and L′ would lead to either: (1) curved plots if the rate of exchange were comparable to the rate of isomerization, or (2) nearly identical rates in the two sets quoted above if exchange were rapid compared to isomerization. Consequently, *isomerization must proceed much faster than exchange; the phosphines do not mix during isomerization.*

The mechanisms proposed previously for isomerization will not accommodate this discovery. The double displacement mechanism[5] (L′ displacing X followed by X displacing L) must lead to exchange at every isomerization. Pseudorotation[3] through trigonal-bipyramidal associated states must involve identity of L and L′ at some point.

We conclude that association[6] of L′ and **1** must result in a distorted pentacoordinate state in which L′ occupies an unique position. This distorted state must be able to undergo fluxional change which interconverts the positions of L and X and, therefore, enables isomerization of **1** into **2**. Attractive models may be found in the recent determinations of the structure of pentacoordinate complexes with d^8 electronic configurations.[8] An interesting trend has emerged in the form of frequent deviations from regular pentacoordinate geometry so that it is often impossible to classify the structure as either trigonal bipyramidal or tetragonal pyramidal. During association and the fluxional change causing isomerization, L′ must retain its identity—perhaps due to a long Pt–L′ bond, as in the complex studied by Meek and Ibers,[8e] or in $Ni(PR_3)_3(CN)_2$,[8c] where one phosphine is unique and has a long Ni–P bond.

The activation enthalpy for isomerization is low, only 3 kcal/mol,[3] and it is considerably higher in displacement reactions.[9] The activation entropy is similar for substitution and isomerization and indicates the importance of association.[2,3] Therefore, isomerization appears to be a low energy process proceeding through a distorted pentacoordinate state. Since some barrier to fluxional change would be expected, the pentacoordinate state may be similar in geometry to that

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[1] Research supported by Grant No. GP-13453 from the National Science Foundation.

[2] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 1st ed, Wiley, New York, N. Y., 1957; 2nd ed, 1967; C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1966.

[3] P. Haake and R. M. Pfeiffer, *Chem. Commun.*, 1330 (1969); for spectra, see P. Haake and T. A. Hylton, *J. Amer. Chem. Soc.*, **84**, 3774 (1962).

[4] There are many more results of this kind; these are two of the most striking.

[5] Discussed in ref 2 and in L. Cattalini and M. Martelli, *J. Amer. Chem. Soc.*, **90**, 4272 (1968).

[6] We have observed kinetic evidence for association with L′ = tricyclohexylphosphine; the observations are similar to those reported in a displacement reaction.[7]

[7] P. Haake, *Proc. Chem. Soc. London*, 278 (1962).

[8] Among the recent reports are: (a) F. K. Ross and G. Stucky, *Inorg. Chem.*, **8**, 2734 (1969); (b) L. P. Haugen and R. Eisenberg, *ibid.*, **8**, 1072 (1969); (c) J. K. Stalick and J. A. Ibers, *ibid.*, **8**, 1084, 1090 (1969); (d) M. DiVaira and P. O. Orioli, *ibid.*, **8**, 2729 (1969); (e) D. W. Meek and J. A. Ibers, *ibid.*, **8**, 1915 (1969).

[9] Reference 2 and G. Carturan and D. S. Martin, *ibid.*, **9**, 261 (1970).

formed on initial association, Displacement appears to involve formation of a considerably higher energy pentacoordinate species.[2,7]

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Temperature Effects on the Luminescence of Benzophenone in Polymers

Sir:

Benzophenone has been studied extensively both as a triplet-state sensitizer and for its photochemical reactivity. Saltiel and coworkers[1] recently reported that in degassed carbon tetrachloride solutions benzophenone and several other ketones exhibit phosphorescence and delayed thermal fluorescence at 296°K. For benzophenone, approximately 10% of the total emission was attributed to delayed fluorescence. Borisevich and Gruzinskii[2] reported earlier a comparable delayed fluorescence for benzophenone vapor. The possible presence of significant populations of excited singlet-state ketone molecules in equilibrium with triplet-state molecules could be of great significance to the photochemistry of these molecules because reactions previously attributed to ketones in their triplet state might actually occur from the excited singlet state.

Although the results of Saltiel, *et al.*, and Borisevich and Gruzinskii are consistent with their interpretation, it is also possible that the "delayed fluorescence" is actually due to thermally activated energy transfer to a diffusing impurity with an excited state of higher energy and shorter lifetime than benzophenone. Indeed, the phosphorescence lifetime of benzophenone in fluid solvents has been shown to vary with concentration,[2,3] and the spectral distribution of the phosphorescence[1-3] does not agree with the previously published low-temperature phosphorescence spectrum.[4] Because of the importance of delayed thermal fluorescence to the interpretation of the photochemistry of benzophenone (and other ketones), we have investigated the effects of temperature on the luminescence of benzophenone in polymers that prevent molecular diffusion. We have been able to establish that benzophenone does emit delayed thermal fluorescence at 300°K and that the spectrum of this emission is an approximate mirror image of the structured singlet–singlet n, π^* absorption spectrum. The use of polymer matrices has also provided insights into the effects of temperature and matrix on the triplet-state lifetime of benzophenone.

Our experimental techniques are essentially the same as reported previously.[5] Spectroquality carbon tetrachloride (MCB) and zone-refined benzophenone (Princeton Organics PAR Grade) were used as received. The emission spectra were corrected for instrument spectral response with an Aminco spectrophotofluorometer (Model 4-8202) having a corrected spectra attachment (Model 4-8210). All of the emission spectra for polymer samples were recorded with a phosphoroscope to exclude scattered excitation.

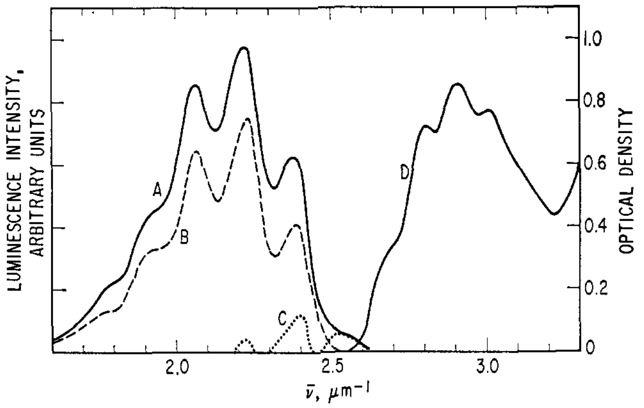

Figure 1. Absorption (curve D) and quanta-corrected delayed luminescence (curves A, B, and C) spectra of benzophenone in polystyrene at 300°K (A and C), 197°K (B), and 77°K (D). Curves A and C are plotted on the same intensity scale. Curve C is the delayed thermal fluorescence spectrum.

Delayed Fluorescence. In agreement with Saltiel, *et al.*,[1] we find that at 300°K the luminescence spectrum of benzophenone in carbon tetrachloride exhibits an extra band on the high-energy side of the phosphorescence, with a peak height roughly $^1/_7$th that of the 0–0 phosphorescence band. In poly(methyl methacrylate), I, poly(α-methylstyrene), II, poly(α,β,β-trifluorostyrene), III, and polystyrene, IV (curve A in Figure 1), at 300°K, we observe the same spectra as in CCl_4, except for a solvent shift. The ratio of the 0–0 phosphorescence band to the 0–3 and 0–4 bands is much larger in our corrected spectra than in the corrected spectra reported by Saltiel, *et al.*,[1] and by Clark, Litt, and Steel.[6] We believe our spectra are the true room-temperature emission spectra because of their agreement (after correction for delayed fluorescence) with the low-temperature spectra in these polymers (curve B in Figure 1) and the agreement of the latter with the previously reported low-temperature phosphorescence spectra.[4] Our observation of the same luminescence spectrum for varying wavelength of excitation (290–360 nm) and for several different rigid polymers rules out the possible contribution of impurities to the spectrum.

The assignment of the band at 2.52 μm^{-1} to delayed fluorescence is reinforced by our observation that it is actually one of several thermally activated emission bands appearing between 2.6 and 2.1 μm^{-1}. The thermally activated component of the emission spectrum (curve C in Figure 1) was obtained: (1) by subtracting from curve A a low-temperature phosphorescence spectrum that was recorded at low resolution to duplicate the band width of curve A and (2) by normalizing the two spectra at 2.07 μm^{-1}, where the relative contribution of the delayed fluorescence is minor. The resulting difference spectrum, which we assign to delayed fluorescence, is in fact an approximate mirror image of the structured singlet–singlet n, π^* absorption spectrum of benzophenone in IV (curve D in Figure 1).

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(1) J. Saltiel, H. C. Curtis, L. Metts, J. W. Miley, J. Winterle, and M Wrighton, *J. Amer. Chem. Soc.*, **92**, 410 (1970).

(2) N. A. Borisevich and V. V. Gruzinskii, *Dokl. Akad. Nauk SSSR*, **175**, 852 (1967); *Proc. Acad. Sci., USSR*, **175**, 578 (1967).

(3) C. A. Parker and T. Joyce, *Chem. Commun.*, 749 (1968).

(4) C. A. Parker, "Photoluminescence of Solutions," American Elsevier, New York, N. Y., 1968, pp 433–434.

(5) P. F. Jones and S. Siegel, *J. Chem. Phys.*, **50**, 1134 (1969).

(6) W. D. K. Clark, A. D. Litt, and C. Steel, *J. Amer. Chem. Soc.*, **91**, 5413 (1969).