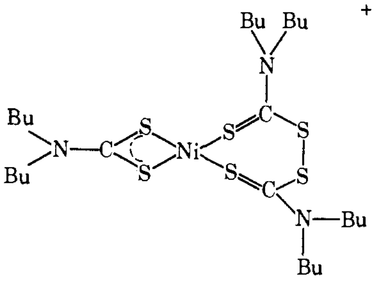
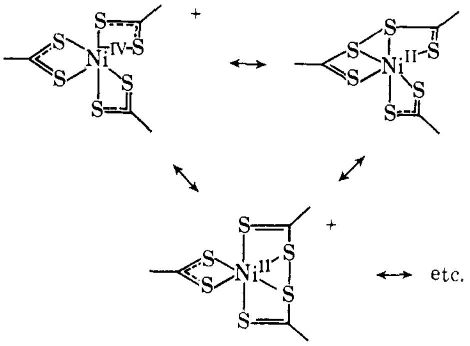
Since transition metal complexes of thiuram disulfide, $[R_2NC(S)S]_2$, have been prepared,[20] it appeared reasonable, in the absence of X-ray structural data, to formulate $Ni(Bu_2dtc)_3^+$ as a planar cationic complex (II) of nickel(II). Indeed thiuram disulfide can be used to prepare compounds having visible and infrared spectra identical with that of the corresponding $Ni(R_2dtc)_3Br$. On addition of the disulfide to a solution of $Ni(Bu_2dtc)_3Br$ photochemical and thermal bleaching is inhibited. The return of the brown color associated with $Ni(Bu_2dtc)_3^+$ is accelerated by adding the disulfide to the bleached solutions. We tentatively ascribe the bleaching to a reduction of the metal to nickel(II) and formation of thiuram disulfide.



II

Recognizing the unequivocal evidence that the nickel in $Ni(Bu_2dtc)_3Br$ is surrounded symmetrically by three formally uninegative dithiocarbamate ligands, the cation clearly is electron deficient relative to normal oxidation states for the elements involved. In looking for reasons for the apparent stability of the cation, it seems plausible that oxidation involving the ligands is important. In a valence-bond description, this may be depicted by resonance structures such as those in eq 2.[21]



(2)

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(21) We acknowledge support from the National Institutes of Health, Grant No. AM-13558-02, and the National Science Foundation, Grant No. GP-11701, for this study.

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Photochemistry of Di-*tert*-butyl Ketone and Structural Effects on the Rate and Efficiency of Intersystem Crossing of Aliphatic Ketones

Sir:

The current communication deals with photochemistry and fluorescence studies of di-*tert*-butyl ketone and their implication on the rate of intersystem crossing of aliphatic ketones.

Photolysis of di-*tert*-butyl ketone (5 g) in pentane (100 ml) with a 200-W Hanovia medium-pressure Hg arc yielded three major organic products, isobutane, isobutylene, and 2,2,3,3-tetramethylbutane, and three minor products, the sum of which accounted for less than 1% of total products.[1] A sizable amount of gas was evolved durng the irradiation (identified as CO by glc on a molecular sieve 5A column). The yield of CO was 90% on the basis of ketone decomposed.

$$(CH_3)_3CCOC(CH_3)_3 \xrightarrow{h\nu} (CH_3)_3CH + (CH_3)_2C{=}CH_2 + (CH_3)_3CC(CH_3)_3 + CO$$

Kinetic analyses were carried out in hexane solution (0.576 M) at 3130 Å with an apparatus previously described.[2] The disappearance of starting ketone follows zero-order kinetics up to 40% conversion. The quantum yield of ketone decomposition using a ferrioxalate actinometer and pinacolone as a secondary standard[3] was found to be 0.71 ± 0.04. Similarly, the quantum yields of CO and 2,2,3,3-tetramethylbutane formation were 0.62 ± 0.03 and 0.10 ± 0.01, respectively. The relative quantum yields of the ketone decomposition in the presence of varying concentration of *cis*-piperylene were determined. The Stern–Volmer plot (Figure 1), as in the case of other *tert*-butyl ketones,[3] is nonlinear. The plot was analyzed as a composite from two linear plots derived from two reactive states, a more readily quenchable state with a slope of 1.10 M^{-1} and a less readily quenchable state with a slope of 0.08 M^{-1}. The quantum yield for ketone decomposition *via* the singlet excited state (ϕ_s) was determined to be 0.31 from the intercept by extrapolating the linear plot of the less readily quenchable state to zero quencher concentration,[4] while the quantum yield for ketone decomposition *via* the triplet state (ϕ_t) was obtained as the difference between ϕ and ϕ_s to be 0.40.

The lifetime of the singlet excited state of di-*tert*-butyl ketone was determined by a double-quenching experiment using biacetyl as the singlet energy acceptor. The quenchers used were mixtures of biacetyl and *cis*-piperylene. The total quencher concentration was maintained at 3 M, while the concentration of biacetyl was varied from 0.025 to 0.15 M. A linear Stern–Volmer plot was obtained by plotting ϕ_0/ϕ against the biacetyl concentration with a slope of 44.5 l. mol^{-1}. Assuming either quencher has equal efficiency as a triplet-state quencher, any quenching with varying concentration of biacetyl will be due to the energy transfer from the singlet excited state of di-*tert*-butyl ketone to biacetyl. Assuming the rate of energy transfer in hexane is 1×10^{10} l. mol^{-1} sec^{-1}, the lifetime of singlet excited state of di-*tert*-butyl ketone is estimated at 4.45 nsec. In a separate experiment of the lifetime of singlet excited state was determined from the fluorescence of di-*tert*-butyl ketone by the single-photon counting technique[5] to 5.6 ± 0.5 nsec. The lifetimes

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(1) The vapor-phase photolysis of di-*tert*-butyl ketone at elevated temperature has been reported by J. W. Kraus and J. G. Calvert, *J. Amer. Chem. Soc.*, **79**, 5921 (1957).

(2) D. R. Coulson and N. C. Yang, *ibid.*, **88**, 4511 (1966).

(3) N. C. Yang and E. D. Feit, *ibid.*, **90**, 504 (1968).

(4) F. S. Wettack, G. D. Renkes, M. G. Rockley, N. J. Turro, and J. C. Dalton, *ibid.*, **92**, 1794 (1970).

of the singlet excited state of di-*tert*-butyl ketone as determined by two different methods thus seem to be in reasonable agreement with each other. The discrepancy may be derived from the assumed rate of energy transfer and (or) experimental error.

The lifetime of triplet state of di-*tert*-butyl ketone was estimated from the slope of an adjusted Stern–Volmer plot of $\phi_t{}^0/\phi_t$ against the *cis*-piperylene concentration to be 0.11 nsec assuming the same rate of energy transfer. The results indicate that di-*tert*-butyl ketone undergoes the type I process with a rate of the order of 6×10^7 sec^{-1} from the singlet excited state and with a rate of $7\text{–}9 \times 10^9$ sec^{-1} from the triplet state; *i.e.*, the type I process occurs much more rapidly from the triplet state than the singlet excited state, an observation in agreement with that of acetone in gas phase[6] and recent work on cyclic ketones in solution.[7] The high reactivity of the triplet state in these cases may be attributed to its geometry,[8] the electrostatic repulsion in the triplet state, or other unknown factors.

Table I

	τ_s, nsec Fluorescence[a]	τ_s, nsec Energy transfer[b]	ϕ_{isc}	k_{isc}, sec^{-1}
Acetone	2.0[c]	1.8[d]	0.90[e]	$4.5\text{–}5.0 \times 10^8$
2-Pentanone	1.8[c]	2.02[f]	0.64[f]	3.1×10^8 [f]
2-Hexanone		0.73[f]	0.27[f]	3.7×10^8 [f]
Cyclopentanone	2.0[g]	1.90[d]		
Pinacolone	4.2[c]	3.16	<0.78	$<1.86\text{–}2.47 \times 10^8$
tert-Butyl *n*-propyl ketone		2.7		
tert-Butyl *n*-butyl ketone		0.68		
Di-*tert*-butyl ketone	5.6	4.45	<0.69	$<1.2\text{–}1.5 \times 10^8$
2,2,5,5-Tetramethylcyclopentanone	8.7[g]			$<1.2 \times 10^8$
Norcamphor	5.2[c]			$<1.9 \times 10^8$
2-Adamantanone	8.0[h]			$<1.25 \times 10^8$

[a] From the single-photon counting technique; error limits, ±10%. [b] Unless otherwise noted, these values were determined from energy transfer to biacetyl in hexane assuming $k_q = 1.0 \times 10^{10}$ l. mol^{-1} sec^{-1}. [c] F. S. Wetlack, G. D. Renkes, M. G. Rockley, N. J. Turro, and J. C. Dalton, *J. Amer. Chem. Soc.*, **92**, 1794 (1970). [d] F. Wilkinson, *Advan. Photochem.*, **3**, 255 (1964). [e] From energy transfer to 3-methyl-2-pentene. [f] N. C. Yang, S. P. Elliott, and B. Kim, *J. Amer. Chem. Soc.*, **91**, 7551 (1969). [g] J. C. Dalton, D. M. Pond, D. S. Weiss, F. D. Lewis, and N. J. Turro, *ibid.*, **92**, 2566 (1970). [h] J. C. Dalton, D. M. Pond, and N. J. Turro, *ibid.*, **92**, 2173 (1970).

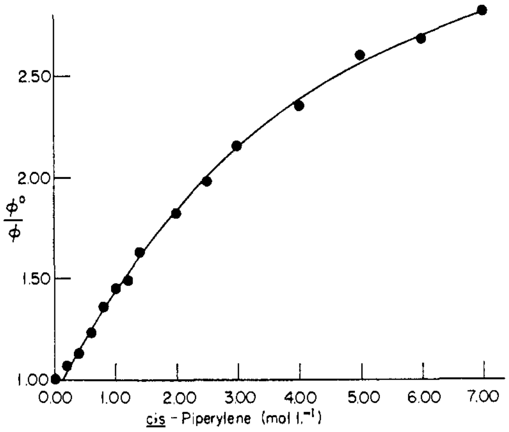

Figure 1.

Since the ϕ_s of di-*tert*-butyl ketone is 0.31 and the fluorescence quantum yield may be estimated at 0.004,[9] the intersystem crossing efficiency (ϕ_{isc}) of di-*tert*-butyl ketone has a limiting value of 0.69. Therefore, the rate of intersystem crossing ($k_{isc} = \phi_{isc}/\tau_s$) has a limiting value of $1.25\text{–}1.55 \times 10^8$ sec^{-1} depending upon the choice of lifetime of singlet excited state from either the fluorescence or energy transfer study.

The principal mode of decay of singlet excited states of aliphatic ketones without γ-hydrogen is believed to be intersystem crossing. The rate of intersystem crossing of acetone and 2-alkanones has been determined to be $3.05\text{–}5.0 \times 10^8$ sec^{-1} (Table I). It is interesting to note that the lifetimes of the singlet excited state of 2,2,5,5-tetramethylcyclopentanone, norcamphor, and 2-adamantanone (Table I) are all appreciably longer than that of acetone. The limiting values for the rates of intersystem crossing of these ketones are $1.2\text{–}1.9 \times 10^8$ sec^{-1}. Therefore, the rates of intersystem crossing of poly α-substituted ketones and constrained bicyclic ketones are appreciably lower than those of straight-chain ketones or unsubstituted alicyclic ketones.

The probability of nonradiative transition among electronic states including intersystem crossing will depend upon the relative positioning of potential energy surface of these states, *i.e.*, the Franck–Condon vibrational overlap factor.[10] In contrast to aromatic hydrocarbons, deuteration of acetone has only relatively minor effect on the fluorescence[11] or phosphorescence[12] of acetone. We have observed that α methylation or confining the carbonyl group in a cage-like ring system increased the lifetime of ^{1}n,π^* and reduced the rate of intersystem crossing of aliphatic ketones, and it has been shown that α methylation may also increase the phosphorescence efficiency by reducing the rate of nonradiative decay of triplet state.[12] These observations suggest that α-C–H stretching may not be the only factor in nonradiative transitions among states of aliphatic ketones. Since the C—H bond in the ^{1}n,π^* of formaldehyde is out of the plane of the C=O group by 20°, while the C—H bond in the ^{3}n,π^* is out of the plane by 35°, it is reasonable to assume that the corresponding

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(5) For a discussion of this technique, see J. B. Birks and I. H. Munro, *Progr. React. Kinet.*, **4**, 215 (1967).

(6) R. B. Cundall and A. S. Davis, *Proc. Roy. Soc., Ser. A*, **290**, 563 (1966).

(7) J. C. Dalton, D. M. Pond, D. S. Weiss, F. D. Lewis, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 2566 (1970).

(8) V. E. DiGiorgio and G. W. Robinson, *J. Chem. Phys.*, **31**, 1678 (1959); G. W. Robinson and V. E. DiGiorgio, *Can. J. Chem.*, **36**, 31 (1968).

(9) A. C. Testa and M. O'Sullivan, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., 1968, PHYS 166.

(10) R. P. Frosch and G. W. Robinson, *J. Chem. Phys.*, **38**, 1187 (1963).

(11) Current results from our laboratories indicated that the τ_s and ϕ_f of acetone-d_6 are about 1.4 ± 0.2 times those of acetone. See also R. F. Borkman and D. R. Kearns, *ibid.*, **44**, 945 (1966).

(12) M. O'Sullivan and A. C. Testa, *J. Amer. Chem. Soc.*, **92**, 258 (1970).

states of aliphatic ketones may also have a somewhat nonplanar geometry. Since factors which may restrain the out-of-plane bending of α-C–C bond of an aliphatic ketone, such as α methylation or confining the carbonyl group in a cage-like system, increase the lifetime of ^{1}n,π^* and reduce the rate of intersystem crossing, the total Franck–Condon factor may well be a product of several terms, and the decrease in the k_{isc} may be due at least in part to the modification in the Franck–Condon factor involving the out-of-plane bending of α-C–C bonds in the various states of aliphatic ketones.

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Rapid Intramolecular Rearrangements in Pentacoordinate Transition Metal Compounds. On the Rearrangement Mechanism of Some Fluxional Iridium(I) Complexes[1]

Sir:

Stereochemical nonrigidity is a characteristic and chemically important feature of pentacoordinate phosphorus(V) compounds,[2] and several elegant studies have recently established a detailed and apparently general molecular rearrangement mechanism.[3] In contrast, although pentacoordination is now well known for transition metal complexes,[4] only a few observations of rapid intramolecular rearrangement in such complexes have been reported.[5] And in no case has information been presented which would distinguish between the theoretically possible polytopal mechanisms for the rearrangement process.[6] We wish to describe a series of iridium(I) complexes, which provide the first such evidence regarding the mechanism of site interchange for a fluxional pentacoordinate transition metal compound.

We have prepared compounds of the type $\mathrm{RIr(COD)P_2}$ (see Table I) by standard methods,[7] and have measured their ^{1}H nmr spectra over a wide temperature range. The numerical results of this study are summarized in Table I, and the spectra we observe for $\mathrm{CH_3Ir(COD)(P(C_6H_5)(CH_3)_2)_2}$ (from −3 to +117°) are presented in Figure 1.

For each compound the low-temperature limiting spectrum shows for the COD ligand two vinylic resonances and two broad methylenic resonances[10] (*e.g.*, $\mathrm{CH_3Ir(COD)(P(C_6H_5)(CH_3)_2)_2}$ at −3° in Figure 1). In addition, the resonance of R appears as a (1:2:1) triplet, indicating equal coupling to the two phosphorus atoms. Furthermore, the phosphine methyl resonances appear as multiplets with pseudotriplet structure, resulting from virtually coupled $\mathrm{X_3AA'X'_3}$ spin systems.[11] For the $\mathrm{P(C_6H_5)(CH_3)_2}$ compounds the diastereotopic[12] methyl groups on each phosphine give rise to a *pair* of multiplets (Figure 1, −3°). On the basis of these and other observations[13] the compounds $\mathrm{RIr(COD)P_2}$ are assigned the (idealized) trigonal bipyramidal (TBP) structure I (see Figure 2).

As the temperature is raised the separate vinylic resonances seen in the limiting spectrum gradually coalesce to a single resonance at the mean. Concomitant averaging of the COD methylene signals also takes place. However, the triplet pattern for R and the pseudotriplet phosphine methyl patterns are maintained throughout, and furthermore, there is *no equilibration of the resonances of the two diastereotopic methyl groups* in the $\mathrm{RIr(COD)(P(C_6H_5)(CH_3)_2)_2}$ compounds (Figure 1, −3 to +87°). Phosphine dissociation, implied by collapse of the structure of the R and phosphine methyl resonances, occurs only at higher temperatures (*e.g.*, 117° for $\mathrm{CH_3Ir(COD)}$-

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[1] Work supported in part by the Petroleum Research Fund.

[2] (a) E. L. Muetterties and R. A. Schunn, *Quart. Rev., Chem. Soc.*, 20, 245 (1966); (b) F. H. Westheimer, *Accounts Chem. Res.*, 1, 70 (1968).

[3] G. M. Whitesides and W. M. Bunting, *J. Amer. Chem. Soc*, **89**, 6801 (1967); G. M. Whitesides and H. L. Mitchell, *ibid.*, **91**, 5384 (1969); D. Gorenstein and F. H. Westheimer, *ibid.*, **92**, 634 (1970).

[4] See ref 2a; also see J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, **8**, 1084 (1969); K. N. Raymond, D. W. Meek, and J. A. Ibers, *ibid.*, 7, 1111 (1968), and references contained therein.

[5] (a) $\mathrm{Fe(CO)_5}$, F. A. Cotton, A. Danti, J. S. Waugh, and R. W. Fessenden, *J. Chem. Phys.*, **29**, 1427 (1958); R. Bramley, B. N. Figgis, and R. S. Nyholm, *Trans. Faraday Soc.*, **58**, 1893 (1962); (b) $\mathrm{Fe(PF_3)_x(CO)_{5-x}}$, C. A. Udovich, R. J. Clark, and H. Haas, *Inorg. Chem.*, **8**, 1066 (1969); $\mathrm{(C_4H_6)Fe(PF_3)_2(CO)}$, J. D. Warren and R. J. Clark, *ibid.*, **9**, 373 (1970); $\mathrm{CF_3Co(PF_3)(CO)_3}$, C. A. Udovich and R. J. Clark, *J. Amer. Chem. Soc.*, **91**, 526 (1969); (c) $\mathrm{HIr(CO)_2(P(C_6H_5)_3)_2}$, G. Yagupsky and G. Wilkinson, *J. Chem. Soc. A*, 725 (1969).

[6] E. L. Muetterties, *J. Amer. Chem. Soc.*, **91**, 4115 (1969).

[7] These compounds were prepared by treating $\mathrm{(Ir(COD)Cl)_2}$ in benzene with the required amount of phosphine ligand (P) and methyllithium or isopropylmagnesium bromide. Satisfactory elemental analyses have been obtained for each compound. The preparation of $\mathrm{HIr(COD)(P(C_6H_5)_3)_2}$ has been reported,[8] but the nmr behavior communicated here has not received prior mention. We had independently prepared this hydride by treating $\mathrm{Ir(COD)(P(C_6H_5)_3)_2{}^+}$ [9] with hydrazine.

[8] (a) H. Yamazaki, M. Takesada, and N. Hagihara, *Bull. Chem. Soc. Jap.*, **42**, 275 (1969); (b) M. Lavecchia, M. Rossi, and A. Sacco, *Inorg. Chim. Acta*, **4**, 29 (1970).

[9] J. R. Shapley, R. R. Schrock, and J. A. Osborn, *J. Amer. Chem. Soc.*, **91**, 2816 (1969).

[10] In some solvents the methylenic resonances are not clearly resolved (*e.g.*, dichloromethane).

[11] R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).

[12] For terminology, see K. Mislow and M. Raban, *Top. Stereochem.*, **1**, 1 (1967).

[13] (a) The separate vinylic resonances have quite different line widths. Since coupling to R is small, this difference must arise from differential coupling to the phosphorus atoms, more in keeping with the TBP structure than with the alternative tetragonal pyramid structure.[8b] We tentatively assign the lower field (broader) signal to the equatorial vinyl protons. (b) The phosphorus–hydride coupling constants (*ca.* 22 Hz) are consonant with those found for similar iridium species with hydride cis to phosphorus (see ref 5c); the phosphine–methyl patterns indicate rather strong P–P coupling, a situation not found for iridium complexes with *cis*-phosphines. (c) We have also prepared the analogous 1,2-diphenylphosphinoethane–hydride complex, and its nmr spectrum is consistent only with a TBP structure. A forthcoming paper will describe other compounds of this type more fully. (d) The compound $\mathrm{Ir(COD)_2SnCl_3}$ has been shown to have a TBP structure, with COD spanning axial–equatorial sites: P. Porta, H. M. Powell, R. J. Mawby, and L. M. Venanzi, *J. Chem. Soc. A*, 455 (1967). (e) An X-ray structure determination is presently in progress to verify this assignment.