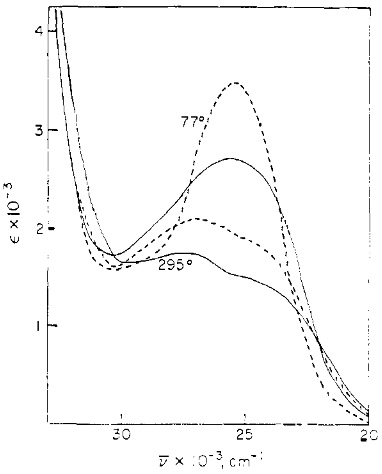

Figure 1. Ligand-field spectrum of $[Ni(CN)_2\{PhP(OEt)_2\}_3]$ as a function of temperature (°K).

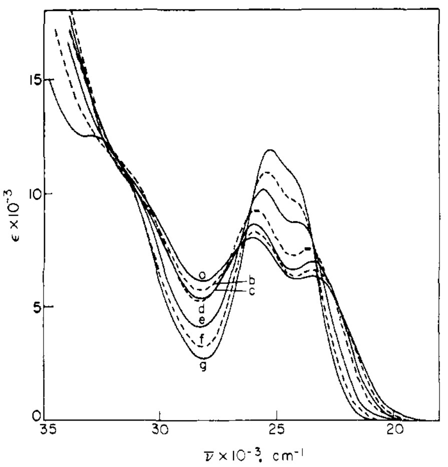

Figure 2. Ligand-field spectrum of [PtCl(QP)]Cl as a function of temperature (°K): a, 295°; b, 258°; c, 207°; d, 156°; e, 132°; f, 119°; g, 100°.

peratures, the actual structure depending on the magnitude of, *e.g.*, solute–solvent interactions at a given temperature. The appearance of ν_1 would then reflect the amount of distortion in this intermediate structure.

The dynamic Jahn–Teller effect could also account for both the splitting of the low-energy band ν_1 and its temperature dependence, provided that the trigonal-bipyramidal complexes have a regular or nearly regular structure in *solution*. Those vibrations which are Jahn–Teller active must have nonvanishing matrix elements of the form $\langle k|\partial\mathcal{H}/\partial Q_i)_0|k\rangle$, where $\mathcal{H}$ is the total Hamiltonian of the system, Q_i is a nuclear displacement, and k represents an electronic state.[10] If $(\partial\mathcal{H}/\partial Q_i)_0$ and $|k\rangle$ transform as components of the irreducible representations Γ' and Γ, respectively, then for matrix elements to be nonzero, Γ' must be contained in the symmetric direct product $[\Gamma]^2$. It is found that in D_{3h} symmetry the three ϵ' vibrations can lift the degeneracy of both E′ and E″ excited electronic states, and that in C_{3v} symmetry the four ϵ vibrations will split the E levels. A system involving interaction of an E electronic level with several doubly degenerate vibrational modes[11] behaves similarly to one involving a single pair of ϵ modes, and the separation $\Delta\nu_1$ of the two components of transition ν_1 is obtained by summing[10,12] over all Jahn–Teller-active $\epsilon(')$ vibrations to give

$$(\Delta\nu_1)^2 = \sum_{i=1}^{n}(2A_i{}^2\hbar/\mu_i\omega_{\epsilon i}) \coth(\hbar\omega_{\epsilon i}/2kT)$$

where $2A$ is the splitting of an E electronic term by unit distortion, μ is the reduced mass of the vibrating atoms, ω_ϵ is the frequency of an $\epsilon(')$ normal mode, and T is the temperature. Thus a decrease in $\Delta\nu_1$ with decreasing temperature is predicted, as is found here.

Finally, it should be noted that preliminary experiments on the solid complexes (in the form of thin films on silica plates) show that there is hardly any change in $\Delta\nu_1$ on lowering the temperature, in marked contrast to the behavior in solution. It appears that in the *solid* state the asymmetry or splitting of ν_1 is due primarily to a ground-state distortion. Full results and a more extensive discussion of the relative merits of the variable ground-state distortion and dynamic Jahn–Teller approaches will be published later.

Acknowledgment. We thank Professor D. W. Meek for several useful discussions and for a gift of some of the nickel complexes, which were analyzed samples prepared by Drs. G. S. Benner and G. Dyer.

James W. Dawson, L. M. Venanzi*
Department of Chemistry
State University of New York at Albany
Albany, New York 12203

James R. Preer, James E. Hix, Jr., Harry B. Gray*
Contribution No. 4156, Arthur Amos Noyes
Laboratory of Chemical Physics
California Institute of Technology, Pasadena, California 91109
Received October 26, 1970

---

(10) M. D. Sturge, *Solid State Phys.*, 20, 91 (1967).

(11) J. C. Slonczewski, *Phys. Rev.*, 131, 1596 (1963).

(12) M. C. M. O'Brien, *Proc. Phys. Soc., London*, 86, 847 (1965).

Secondary Deuterium Isotope Effects on Triplet Excitation Transfer. Deuterium Position and Sensitizer Effects

Sir:

Secondary deuterium isotope effects have been found useful in understanding bimolecular photochemical interactions.[1–3] We have previously examined isotope effects in an excitation-transfer system, the photosensitized trans–cis isomerization of β-methylstyrene.[1] We now report extension of those studies to include other sensitizers and other positions of label in β-methylstyrene. The following principal conclusions result: (1) the isotope effect on partitioning of the olefin triplet to cis and trans ground states is nil; (2) significant involvement of remote positions in the excitation-transfer process occurs; (3) sensitizers with widely differing types of chromophore show essentially identical isotope effects, emphasizing the similarity of the bimolecular interactions; and (4) the origins of the deuterium isotope effect are probably more closely allied with the effect of deuterium on excitation en-

---

(1) R. A. Caldwell and G. W. Sovocool, *J. Amer. Chem. Soc.*, **90**, 7138 (1968).

(2) M. W. Schmidt and E. K. C. Lee, *ibid.*, **90**, 5919 (1968).

(3) (a) R. A. Caldwell and S. P. James, *ibid.*, **91**, 5184 (1969); (b) R. A. Caldwell, *ibid.*, **92**, 1439 (1970).

Table I. Photosensitized Isomerization of *trans*-β-Methylstyrene to the Cis Form

Sensitizer (E_T, kcal/mol)	β[a]	α[a]	Para[a]	Meta[a]	% cis, photostationary state[b]
Propiophenone (74.6)	1.00	0.99			55.0
Benzophenone (68.5)	0.98				64.1
2-Acetonaphthone (59.3)	1.13[c]				86.8
Chrysene (56.6)	1.13	1.05	1.04		*Ca.* 87.5
Biacetyl (54.9)	1.14[d]	1.05	1.05	1.01	88.5
Fluorenone (53.3[e])	1.15[d]	1.08	1.06	1.02	83.2

[a] Values given are: [undeuterated/deuterated cis product]/[undeuterated/deuterated trans starting material]. Experimental error in all cases is *ca.* ±0.015–0.02 as judged either from the reproducibility of the low-voltage mass spectral analysis or from agreement between replicate experiments. [b] Experimental error *ca.* 5% in the cis:trans ratio, measured *via* gas chromatography. [c] Single determination. [d] R. A. Caldwell and G. W. Sovocool, *J. Amer. Chem. Soc.*, **90,** 7138 (1968). [e] K. Yoshihara and D. R. Kearns (*J. Chem. Phys.*, **45,** 1991 (1966)) suggest a lower value, but the value we choose is in better accord with other kinetic data; *cf.* W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, **88,** 4769 (1966).

ergy[2] than with the effect on Franck–Condon factors associated with twisting around the α,β bond in the olefin T_1 state.[1]

Samples of *trans*-β-methylstyrene specifically labeled with deuterium in the β, α, meta, or para position were prepared, diluted with unlabeled material, and photoisomerized partly (5–10%) to cis in outgassed benzene solution *via* irradiation of the sensitizers in Table I at 366 or 436 nm. The ratios given in Table I are, as before,[1] the product of the isotope effect on the excitation-transfer step and the isotope effect on partitioning of the olefin triplet between cis product and trans starting material. Since excitation transfer is expected to be diffusion controlled from benzophenone and propiophenone triplets to *trans*-β-methylstyrene (E_T 59.8 kcal/mol), no isotope effect is expected on the excitation-transfer term. The very small isotope effects in these two cases, thus, clearly point to an isotope effect on triplet partitioning that is well within experimental error of unity, consistent with observations for labeled stilbene.[4] The remaining values in Table I thus reflect only the excitation-transfer term, since the triplet partitioning term is the same in all cases.

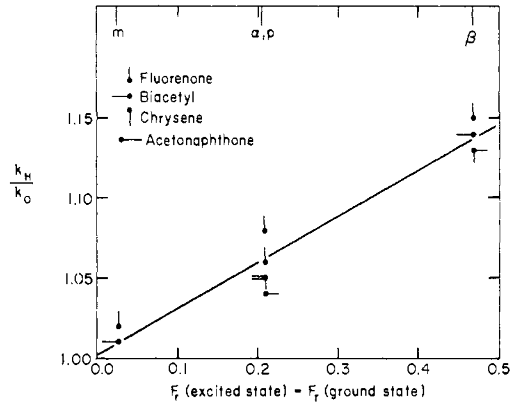

Figure 1. Correlation of isotope effect with change in free-valence index upon excitation.

For the lower energy sensitizers a quite striking similarity appears in the isotope effects as the sensitizer is varied. Note that 2-acetonaphthone and fluorenone are ketones with π–π* lowest triplet states, chrysene is an aromatic hydrocarbon with excitation necessarily in a hydrocarbon π system, and biacetyl has an n–π* lowest triplet. We interpret our results to mean that specific bonding effects between a sensitizer and an acceptor are generally minimal in the excitation-transfer process, since differences in the isotope effects with these widely different sensitizers might otherwise have been expected. Where specific effects are observed,[3,5] we point out that electronic excitation transfer will not be the expected end result of the bimolecular interaction.

Particularly striking also are the large isotope effects associated with para deuteration, k_H/k_D = 1.05. We believe this to be the largest para isotope effect known for any benzene side-chain reaction; *cf.*, for nonphotochemical examples, k_H/k_D = 0.990 ± 0.002 per D for the solvolysis of $(p\text{-DC}_6\text{H}_4)_2\text{CHCl}$,[6] K_H/K_D = 0.98 ± 0.02 for equilibrium acidity of the 2,6-dimethylanilinium-*4-d* ion,[7] and k_H/k_D = 1.018 ± 0.002 for the effect of para deuterium in the lithium cyclohexylamide catalyzed exchange of toluene-α-*d*.[8] Such a large isotope effect can only be ascribed to involvement of the para position nearly as intimately in the excitation-transfer process as the α position, where values for k_H/k_D average 1.06. It is obviously not feasible to associate the para isotope effect with the geometry changes expected around the α,β bond on excitation;[1] the similar magnitude of the α isotope effect thus makes questionable the importance of the expected change toward twisted geometry about the α,β bond to the origin of these isotope effects.

We wish to point out the very good correlation (Figure 1) of the isotope effect at atom r for the lower energy sensitizers with the change in free valence index, F_r,[9] as calculated for styrene by HMO[10] for going from ground state to first excited state, *keeping planar geometry about the α,β bond.* This correlation thus suggests vertical excitation transfer to a planar olefin species. It allows the prediction that comparison with similar experiments with "nonvertical" excitation transfer systems may shed considerable light on the nature of the latter process. We are encouraged in our assignment of *trans*-β-methylstyrene as a vertical acceptor by comparison of the rate constants[11] for its

---

(4) J. Saltiel, *J. Amer. Chem. Soc.*, 89, 1036 (1967).

(5) N. C. Yang, J. T. Cohen, and A. Shani, *ibid.*, 90, 3264 (1968).

(6) A. Streitwieser, Jr., and H. S. Klein, *ibid.*, 86, 5170 (1964).

(7) E. A. Halevi, *Progr. Phys. Org. Chem.*, 1, 109 (1963).

(8) A. Streitwieser, Jr., and J. S. Humphrey, Jr., *J. Amer. Chem. Soc.*, 89, 3767 (1967).

(9) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, p 328 ff.

(10) E. Heilbronner and P. Straub, "Huckel Molecular Orbitals," Springer-Verlag, New York, N. Y., 1966.

(11) Measured by irradiation at 436 nm in the presence of anthracene, assigned a rate constant of 5 × 10^9 M^{-1} sec^{-1} as quencher for sensitizer triplets.

quenching of fluorenone triplets (6.5 kcal endothermic, $k = 1.1 \pm 0.2 \times 10^6\ \text{sec}^{-1}$) and biacetyl triplets (5 kcal endothermic, $k = 8 \pm 2 \times 10^6\ \text{sec}^{-1}$) with data[12] for *trans*-stilbene (a vertical[12] acceptor) quenching triplet sensitizers of comparable endothermicity. There the data indicate estimated rate constants of *ca.* $8 \times 10^5\ M^{-1}\ \text{sec}^{-1}$ for 6.5 kcal endothermicity and *ca.* $5 \times 10^6\ M^{-1}\ \text{sec}^{-1}$ for 5 kcal endothermicity, in close parallel to the values we observe.

Elimination of twisting of the α,β bond as a possible source of the kinetic isotope effects leaves the isotope effect on triplet excitation energy, known for ethylene and aromatic hydrocarbons,[13,14] as the odds-on candidate.[2] The origin of this isotope effect is somewhat obscure, though it must be related to changes in vibrational zero-point energy on going from S_0 to T_1[13c] (or S_1[14]). We have performed some calculations of zero-point energies related to the S_0–T_1 (or S_0–S_1) excitation of benzene and benzene-d_6 by use of a program devised by Boyd.[15] Reasonable changes in obvious force constants (C–C stretch and CC–CC torsion), with all C–H force constants kept constant, give isotope effects on the excitation energy that are only in the range of $10\ \text{cm}^{-1}$, more than an order of magnitude lower than the observed[13c,14] $200\ \text{cm}^{-1}$. We therefore believe that these isotope effects must reflect a significant change in some force constant directly associated with the C–H bond. Of the three possible local modes, the C–H out-of-plane bend seems more plausible than either the stretch or the in-plane bend. On this basis, the correlation of isotope effect with F_r follows logically (though not uniquely) from the expectation that this force constant at atom r will parallel total π-bond order at r ($= \sqrt{3} - F_r$) as a measure of resistance within the π system to out-of-plane deformation at that atom.

Acknowledgment. Acknowledgment is made to the National Science Foundation (Grant GP-14796) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant 3031-A4), for financial support.

---

[12] W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4769 (1966).

[13] (a) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 297, and references; (b) W. Siebrand, *J. Chem. Phys.*, 47, 2411 (1967); (c) G. C. Nieman and D. S. Tinti, *ibid.*, 46, 1432 (1967); D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

[14] F. M. Garforth, C. K. Ingold, and H. G. Poole, *ibid.*, 508 (1948).

[15] R. H. Boyd, *J. Chem. Phys.* 49, 2574 (1966). We thank Professor C. F. Wilcox for assistance with these calculations.

[16] Procter and Gamble Fellow, 1968–1969.

Richard A. Caldwell,* G. W. Sovocool,[16] R. J. Peresie
Department of Chemistry, Cornell University
Ithaca, New York 14850

Received November 6, 1970

Organic Fluorine Compounds. XXXII.[1] Protonated Fluoromethyl Alcohol

Sir:

Formation of fluoromethyl alcohol, **1** (FCH$_2$OH), from ethyl fluoroformate and from formyl fluoride was reported by Olah and Pavlath[2] in 1953. They were, however, unable to isolate and characterize the pure compound. Andreades and England[3] in 1961 prepared a number of highly fluorinated α-fluoro alcohols. Weinmayer[4] in 1963 studied the reaction of fluoroolefins with formaldehyde in hydrogen fluoride and suggested that a solution of paraformaldehyde in hydrogen fluoride contains an equilibrium of 25–30% fluoromethyl alcohol and 70–75% bis(fluoromethyl) ether. Olah and Tolgyesi[5] in 1964 reviewed the haloalkylation reactions and discussed the available literature on α-halo alcohols. The nature of solutions of paraformaldehyde in anhydrous HF, including nmr and other available data for this system, was discussed. It was pointed out that a polymeric fluorohydrin [HO(CH$_2$O)$_n$-CH$_2$F] is formed which reacts similarly to fluoromethyl alcohol under acid-catalyzed conditions. German and Knunyantz in a recent review article[6] discussed reactions of paraformaldehyde in hydrogen fluoride, with particular emphasis on their own earlier work in the field. Fluoromethyl alcohol recently aroused substantial theoretical interest as a model compound for *ab initio* calculations.[7]

We wish now to report the preparation of protonated fluoromethyl alcohol, **2**, through the reaction of formaldehyde with HF–SbF$_5$ and HFSO$_3$–SbF$_5$ in SO$_2$ClF solution and its nmr spectroscopic characterization in these superacid solutions.

When monomeric formaldehyde (generated by thermal depolymerization of paraformaldehyde) is dissolved in a 3:1 (v/v) HF–SbF$_5$ solution at −78° a white precipitate is formed (probably a polymeric formaldehyde product). This precipitate is partly dissolved when the temperature is increased to −40°. The clear supernatant consists of a saturated solution of fluoromethyl alcohol, **1**, in its stable protonated form **2**.

$$\mathrm{CH_2O + HF \longrightarrow \underset{\mathbf{1}}{FCH_2OH} \xrightarrow[\mathrm{SbF_6^-}]{\mathrm{H^+}} \underset{\mathbf{2}}{FCH_2OH_2^+\ SbF_6^-}}$$

The pmr spectrum of **2** (Figure 1a) clearly demonstrates the structure. The methylene signal appearing at δ 6.15 (from capillary TMS) is a doublet ($J_{\mathrm{HF}}^{\mathrm{gem}} = 47.9$ Hz) of triplets $J_{\mathrm{HH}}^{\mathrm{vic}} = 4.9$ Hz). The OH$_2$ triplet ($J_{\mathrm{CH_2OH_2}} = 4.9$ Hz) at δ 12.34 exhibits further splitting (1.7 Hz) due to the corresponding fluorine–proton vicinal coupling. The ^{19}F spectrum (Figure 1b) shows a triplet of triplets with the above-mentioned coupling constants. The fluorine chemical shift is ϕ 166.7 ppm (from CCl$_3$F), a value comparable with that obtained for FCH$_2$OCH$_3$ (ϕ 163.7).[8]

When formaldehyde is dissolved at −78° in 1:1 HFSO$_3$–SbF$_5$/SO$_2$ClF a stable solution of protonated formaldehyde, **3** (hydroxycarbonium ion),[9] is formed. Upon addition of fluoride ion (in the form of sodium

---

[1] Part XXXI: G. A. Olah and P. Kreienbuhl, *J. Org. Chem.*, **32**, 1614 (1967).

[2] G. A. Olah and A. Pavlath, *Acta Chim. Acad. Sci. Hung.*, 3, 203, 425 (1953).

[3] S. Andreades and D. C. England, *J. Amer. Chem. Soc.*, **83**, 4670 (1961).

[4] V. Weinmayer, *J. Org. Chem.*, **28**, 492 (1963).

[5] G. A. Olah and W. S. Tolgyesi in "Friedel-Crafts and Related Reactions," G. A. Olah, Ed., Vol. III, Interscience, New York, N. Y., 1964, pp 737–753.

[6] L. S. German and I. L. Knunyantz, *Angew. Chem.*, 81, 321 (1969), and references therein.

[7] I. G. Csizmadia, Joint Conference of the Chemical Institute of Canada and the American Chemical Society, Toronto, Can., June 1970, Abstracts, ORGN 4; J. A. Pople, Abstracts, ORGN 6.

[8] Prepared by the metathetic reaction of ClCH$_2$OCH$_3$ with HgF$_2$: $\delta_{\mathrm{CH_2}}$ 4.69; $\delta_{\mathrm{CH_3}}$ 3.02; $J_{\mathrm{HF}}^{\mathrm{gem}} = 57$ Hz; $J_{\mathrm{HF}}^{\mathrm{vic}} = 16$ Hz.

[9] G. A. Olah, D. H. O'Brien, and M. Calin, *J. Amer. Chem. Soc.*, **89**, 3582 (1967); A. M. White and G. A. Olah, *ibid.*, **91**, 2943 (1969).