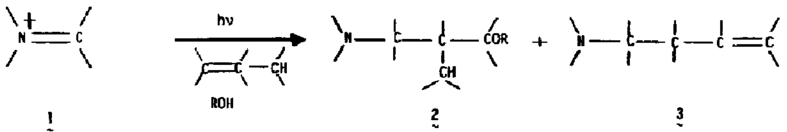
Tetrahedron Letters Vol. 21, pp 3455 - 3458
0040-4039/80/0901-3455$02.00/0

PHOTOCHEMISTRY OF IMINIUM SALTS IN THE PRESENCE OF N-ELECTRON DONATING ALCOHOLS AND ETHERS.[1]

Jerome Stavinoha, Elliott Bay, Andrea Leone and Patrick S. Mariano*,[2]
Departments of Chemistry, University of Maryland, College Park, MD 20742 and
Texas A&M University, College Station, TX 77843

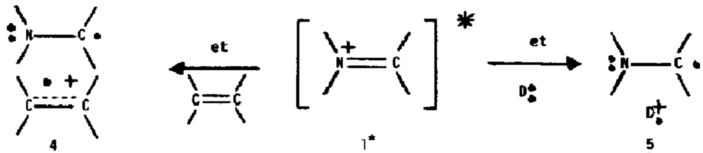
Irradiation of 2-phenyl and 2-isobutenyl-1-pyrrolinium salts in solutions of alcohols and ethers containing α-hydrogens leads to production of addition products. In addition, alcohols and ethers having low ionization potentials and α-hydrogens serve as efficient quenchers of fluorescence from 2-phenyl-1-pyrrolinium salts. Deuterium isotope effects on fluorescence quenching rate constants appear to implicate electron transfer mechanisms in photoaddition and quenching pathways.

Our previous studies have shown that iminium salts undergo photoaddition reactions with electron rich olefins (1 → 2+3) via electron transfer mechanisms[3] in which iminium salt excited states undergo one-electron reduction.[3-5] For these intra- and intermolecular olefin-iminium salt additions, the alkene moiety serves as a π-donor (1→4). A preliminary appraisal indicates that electron rich, n-electron donors should display similar behavior (1 → 5).[6] Reported here are the results of investigations which support this proposal.



1 2 3

Irradiation of alcoholic or ethereal solutions of iminium salts leads to formation of addition products. For example, irradiation of 2-phenyl-1-pyrrolinium perchlorate 6[3b] in THF (Corex, 14.7mM) gave after basic work-up and molecular distillation a 1.2:1 mixture of the diastereomeric 2-tetrahydrofuranyl-phenylpyrrolidines 9 (42%, ϕ=0.015).[7] The photoadduct 10 is produced (43%, ϕ=0.011) when a methanolic solution of the N-methylpyrrolinium salt[7] 7 is irradiated

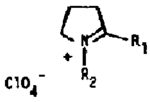


4 1* 5

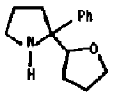
(Corex, 4.0mM). Similar types of addition products are obtained from photoreactions of 6 (12, 15% ϕ=ca. 0.0005) and 8 (10, 43%) with methanol. The bicyclic oxazolidine 12, analogous to products observed by Schmid and his co-workers[8], most probably arises through secondary reaction of the initially formed aminol 11 with formaldehyde, a product of methanol photoxidation.[6b]

A comparison of rate constants for fluorescence quenching (Table 1) by alcohols and ethers provides information about the detailed mechanisms for quenching and reaction. Two trends are noticeable. First, a loose correlation exists between observed kq and free energy for electro transfer to 6^{S_1}, calculated[4] using estimated one-electron oxidation potentials of the alcohols and reduction potential (-0.99V vs SCE in CH_3CN) and singlet energy (89 kcal/mol) of 6. Secon the small yet finite value of kq for t-butyl alcohol indicates that α-CH bond cleavage, a requisite step in photoaddition pathways, is also part of the quenching mechanism.[10]

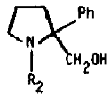
Two limiting mechanisms are possible for quenching and photoaddition processes, one invol ing hydrogen atom transfer and the other sequential electron-proton transfer (Scheme 1). For both, a large degree of reversibility is required at one or more intermediate stages since quenching efficiencies are greater than those for photoaddition. Importantly, the sequential mechanism would rationalize why (1) alcohol quenching rate constants are dependent upon both electron transfer and hydrogen atom donating abilities, and (2) t-butyl alcohol serves as quencher.[11] Distinction between the two mechanisms can be made by use of CD and OD deuterium isotope effects, Hydrogen atom abstractions from alcohols and ethers display normal primary α-CH deuterium isotope effects (k_H/k_D ~ 3).[12] In contrast, small k_H/k_D ratios are observed for OD substitution in processes involving one electron oxidation of alcohols.[6b,13] The measured k_{qCl} k_{qCD} and k_{qOH}/k_{qOD} ratios[14] (Table 2) appear to be in complete accord with pathways for quenching in which electron transfer and proton transfer both contribute to the overall rate (sequential mechanism).



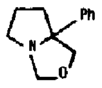
6 R_1=Ph, R_2=H
7 R_1=Ph, R_2=CH_3
8 R_1=CH=C$(CH_3)_2$, R_2=H



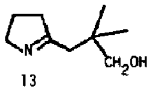
9



10 R_2=CH_3
11 R_2=H

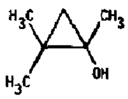


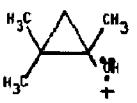
12

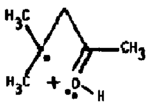


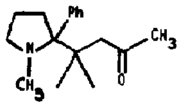
13

In the sequential mechanism, partitioning of the initially formed cation-radical pair occurs by excited state producing, back electron transfer (bet*)[15] in competition with decay t ground state (bet) or proton transfer (H^+). Accordingly, we would expect that the availabilit of low energy reaction pathways following electron transfer (eg. proton transfer) would lead t more efficient quenching. The validity of this hypothesis was tested using 1,2,2-trimethylcyclopropanol (14).[16] This substance, serves as an excellent quencher for the fluorescence of and 7 (k_q=5.10 ± 0.3 x 10^9 $M^{-1}\cdot sec^{-1}$ and 3.1 ± 0.2 x 10^9 $M^{-1}\cdot sec^{-1}$, respectively). The small OD isotope effect observed (1.04 ± 0.06 and 1.06 ± 0.06 for 6 and 7) suggests that a hydrogen atom abstraction mechanism similar to that operable in reaction of 14 with triplet excited ketones[7] where k_H/k_D ~ 5 is not involved in the present case. The question of why the tertiar alcohol 14 serves as an efficient quencher of iminium salt fluorescence is related to the avai ability of a facile C-C bond cleavage reaction forming 16 from the initial cation radical 15. Consistent with this rationale is the observation that the addition product 17[7] is produced by irradiation of 7 in CH_3CN solutions of 14 (0.63M). Together the results presented above offer strong support for an electron-proton transfer mechanism for alcohol and ether quenching and reaction with iminium salts.


14


15


16


17

Acknowledgements. Generous support of these studies by the Robert A. Welch Foundation and National Institutes of Health (GM 27251) is greatfully acknowledged. We thank Dr. Richard Meyer for the use of his spectrofluorometer.

Table I. Fluorescence Quenching Data for 2-Phenyl-1-pyrrolinium Perchlorate (6).

Quencher	Estim. $E_{½}$ (+)[a] (V)	Estim. ΔG_{et}[d] (kcal/mol)	Obsd. k_q[e] ($M^{-1} \cdot sec^{-1}$)
CH_3OH	3.8	+21	$6.5 \pm 0.3 \times 10^7$
CH_3CH_2OH	3.5	+15	$2.0 \pm 0.1 \times 10^8$
$(CH_3)_2CHOH$	3.2	+8	$7.3 \pm 0.4 \times 10^8$
$(CH_3)_3COH$	2.5	-9	$1.9 \pm 0.1 \times 10^7$
p-dioxane	2.0[b]	-20	$3.7 \pm 0.1 \times 10^9$
THF	1.9[c]	-22	$4.1 \pm 0.2 \times 10^9$

(a) Calculated from ionization potentials[9c] using the method of Miller.[9a] (b) From C.K. Mann and K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel-Dekker, NY, 1970. (c) Estimated by comparison to p-dioxane. (d) Calculate using the method of D. Rehm and A. Weller.[4] (e) Measured in CH_3CN, 25°C with [6] ca. 1 x 10 M; data for 6 are $\phi_f \sim 1.0$, τ=6 ns.

Table II. Fluorescence Quenching Isotope Effects.

Quencher	k_qCH/k_qCD[a]	k_qOH/k_qOD[b]
CH_3OH	1.15	1.36
CH_3CH_2OH	--	1.41
$(CH_3)_2CHOH$	1.12	1.25
$(CH_3)_3COH$	--	1.54
THF	1.20	--

(a) Isotopically labeled compounds used are included in ref 14; no N-D isotope effect was noted for ϕ_f or k_q; error limit in the data is ± 0.06; solvent CH_3CN. (b) Solvent was either 10% H_2O-CH_3CN or 10% D_2O-CH_3CN.

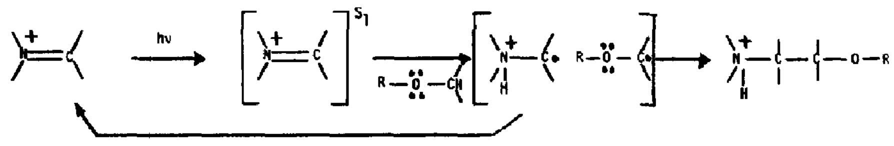
REFERENCES

1. These studies were reported at the 179th National ACS meeting, Houston, 1980, ORGN-148.
2. Current address, Department of Chemistry, University of Maryland.
3. (a) P.S. Mariano, J. Stavinoha and R. Swanson, J. Amer. Chem. Soc., 99, 6781 (1977); (b) P.S. Mariano, J. Stavinoha, G. Pepe and E. Meyer, ibid., 100, 7114 (1978); (c) P.S. Mariano

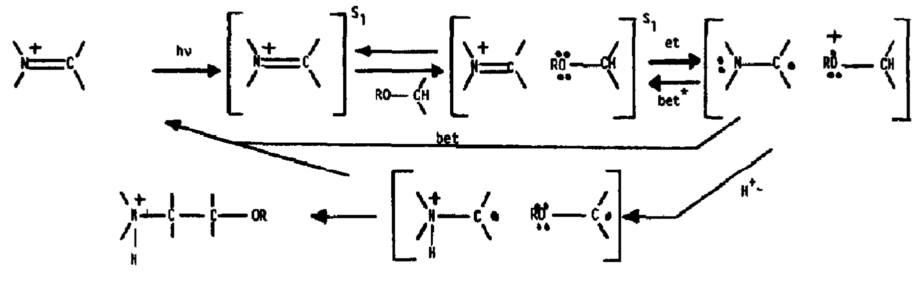
J. Stavinoha and T. Tiner-Harding, Joint ACS-JCS Photochemistry Symposium, Div. of Petr. Chem., General Paper. 24, 78 (1979).

4. (a) D. Rehm and A. Weller, Isr. J. Chem., 8, 259 (1970); (b) F.S. Scandola and V. Balzani, J. Amer. Chem. Soc., 101, 6140 (1979).
5. Excellent reviews of electron transfer in excited chemistry are found in M. Gordon and W.R. Ware, The Exciplex, Acad. Press, N.Y., 1975 and R.S. Davidson in Molecular Association, ed., R. Foster, Acad. Press, N.Y., 1975, ppg 216-318.
6. (a) Electron transfer mechanisms have been proposed for alcohol quenching of singlet states of salts of mono-azaaromatic compounds; (b) A. Ledwith, P.J. Russell and L.H. Sutcliffe, Proc. R. Soc. Lond., A 332, 151 (1973) and references therein; (c) A. Castellano, J.P. Catteau and A. Lablache-Combier, Tetrahedron, 31, 2255 (1975).
7. All new compounds gave satisfactory elemental analyses or high resolution mass spec. derived molecular formulae.
8. H. Goth, P. Cerrutti and H. Schmid, Helv. Chim. Acta., 50, 1759 (1967).
9. (a) L.L. Miller, G.D. Nordblom and E.A. Mayeda, J. Org. Chem., 37, 916 (1972); (b) the relative ordering of $E_{\frac{1}{2}}(+)$ for the alcohols is most probably correct but the absolute magnitudes may be in error; (c) K. Watanabe, J. Chem. Phys., 26, 542 (1957).
10. Irradiation of 6 in t-butyl alcohol for 6h gives disappearance of 6 but no detectable photoproducts. Also, 2,2,4-trimethylpentane does not serve as a quencher for fluorescence of 6.
11. This methanism rationalizes the observed solvent polarity dependence of k_q by CH_3OH (~6 x 10^7 $M^{-1} \cdot sec^{-1}$ in CH_3CN and ~6 x 10^8 $M^{-1} \cdot sec^{-1}$ in 5-40% H_2O-CH CN).
12. H. Paul, R.D. Small and J.C. Sciano, J. Amer. Chem. Soc., 100, 4520 (1978).
13. B.L. Poh and R. Stewart, Can. J. Chem., 50, 3432 (1972).
14. The following CH/CD pairs were used: CH_3OH/CD_3OH, $(CH_3)_2CHOH/(CD_3)_2CDOH$, THF/$d_6$-THF.
15. Back electron transfer generating S^1 (bet*) would be a rapid process when forward electron transfer is endothermic.[4]
16. C.H. De Puy, W.C. Arnez and D.H. Gibson, J. Amer. Chem. Soc., 90, 1830 (1968).
17. C.H. De Puy, H.L. Jones and W.B. Moore, ibid., 95, 477 (1973).

Scheme I. HYDROGEN ATOM TRANSFER



ELECTRON PROTON TRANSFER



(Received in USA 13 May 1980)