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PHOTOREACTIONS OF BIACETYL AND TETRAMETHYLETHYLENE. SOLVENT AND TEMPERATURE EFFECTS.

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Abstract: The photoreaction of biacetyl and tetramethylethylene yields four products (1-4). A substantial variation in product yield and quenching kinetics with temperature and isotopic substitution is found for this photoreaction.

Introduction. The photoreaction of biacetyl with alkenes sometimes yields products[1] derived from an intermediate diradical formed by addition of the carbonyl oxygen atom to the C=C bond, i.e., oxetanes by cyclization and ketone-enol ethers by disproportionation. Generally, the rate constant for hydrogen atom abstraction by n,π* states of ketones from alkenes is expected to be at least an order of magnitude slower than the observed quenching constants.[2] It was surprising, therefore, to observe (eq. 1) substantial yields of products formally derived from hydrogen atom abstraction in the photoreaction of biacetyl (BA) with tetramethylethylene (TME). As a result, we undertook an investigation of solvent, isotope, and temperature effects of product formation and of the solvent and isotope effects on the kinetics of quenching in order to gain some insight to the mechanism of these photoreactions.

Results: product studies. Photoexcitation (435 nm) of biacetyl (BA) in various solvents (hexane, acetonitrile, benzene) containing tetramethylethylene (TME) results in formation of the 1 to 1 adducts 1-4 (eq. 1).[3] Inspection of the structures of the adducts allows their classification into two categories (eq. 2): Enol ethers which may be viewed as arising from an initial addition of an n,π* excited state of BA to TME to produce a diradical intermediate, 5, which partitions itself via disproportionation to 1 and 2 (Type A products) and enols which may be viewed as arising from an initial hydrogen abstraction from TME by an n,π* excited state of BA to produce a radical pair, 6, which partitions itself via disproportionation to 3 and 4 (Type B products). The ratio of products is sensitive to solvent, temperature and deuteration of TME but is not sensitive to the extent of conversion at low (<20%) conversions or to the concentration of TME. Table 1 provides a summary of the variation of products with these parameters. The chemical yields of products 1-4 were high (>70%) in acetonitrile and in benzene, but were low (15-20%) in n-C_6H_{14}. Since it was found that biacetyl disappearance in n-C_6H_{14} was greater in the absence of TME than in its presence, it appears that quenching of BA triplet by TME (which is substantial under the standard conditions of photolysis, see the next section) does not result in efficient formation of products, and that reaction of BA triplets with n-C_6H_{14} is important.

Results: kinetic studies. For concentrations of TME $\leq$ 0.1 M, the singlet state of BA is inefficiently quenched (i.e., BA fluorescence quantum efficiency and fluorescence lifetime do not change significantly upon addition of up to ∿0.1 M TME). On the other hand, the triplet stat of BA is readily quenched by addition of TME. Stern-Volmer analysis of the quenching of biacetyl phosphorescence leads to the kinetic data listed in Table 2. As a check, the quantum efficiency of disappearance of BA in CH_3CN was measured as a function of [TME] and the result were subjected to a Stern-Volmer analysis. The resulting Stern-Volmer constant of 1100 M^{-1} i in good agreement with the value of 1020 M^{-1} derived from phosphorescence quenching. In the case of BA and TME in C_6H_6 values of 78 M^{-1} and 60 M^{-1} are found from quantum yield quenchin plots and phosphorescence quenching plots, respectively.

Conclusion. The salient and unusual results listed in Table 1 and 2 are (1) the strong solve and deuterium isotope dependence of the ratio of Type A to Type B products; (2) the lack of a substantial deuterium isotope effect on the quenching constant in CH_3CN, but the occurrence c a significant effect in C_6H_6 and n-C_6H_{14}; (3) the lack of a substantial temperature effect or the ratio of A/B in CH_3CN, but the occurrence of a large effect in n-C_6H_{14}.

To interpret these results we postulate that the quenching of BA triplets by TME in CH_3(produces an exciplex as a result of charge transfer interaction. In the extreme case, a full electron transfer would occur resulting in a radical cation-anion pair, $D_{\pm}$ (eq. 3). This pos tulate explains the lack of a significant deuterium isotope effect on the quenching step. Hc ever, the partitioning of $D_{\pm}$ to products requires a hydrogen transfer at some point. Thus, t ratio of A/B shows a significant deuterium isotope effect.

In solvents less polar than CH_3CN the charge transfer quenching mechanism is expected to come less favorable. This is confirmed by the decreases in quenching rate constants in C_6H_6 n-C_6H_{14}. In sufficiently non-polar solvents direct hydorgen abstraction may compete with exc plex formation. Indeed, in n-C_6H_{14} the rate constant is not only relatively slow, but a strc deuterium isotope effect on the quenching rate constant is observed. In methanol and t-butan rate constants for quenching by TME of the order of 10^7 M^{-1} sec^{-1} are found.

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References.

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(2) (a) For a review of the rate constants for quenching of biacetyl triplets see: N.J. Turr "Modern Molecular Photochemistry," Benjamin/Cummings, Menlo Park, 1978, p. 378 and p. 437 and associated references. Also see J. Scaiano, J. Photochem., 2, 81 (1973/74
(b) B.M. Monroe, Advances in Photochem., 8, 77 (1971); M.B. Rubin, Fortschritte der Chem. Forschung, 13, 251 (1969); and M.B. Rubin, Chem. Rev., 75, 177 (1975).

(3) The adducts 1, 2, 3 and 4 were unequivocally established by a combination of proton NMR, and MS methods. The percent deuterium content of the $(CD_3)_2C{=}C(CD_3)_2$ was found to conta <1% protons by NMR spectroscopy. Phosphorescence lifetimes were measured by time correla single photon counting on a Photochemical Research Associates device. The nanopulser of latter was modified with a 6 KV, 6 PF capacitor which allowed the generation of 0.1 μs pulses at 1000 Hz.

(4) We thank Prof. G. Jones (Boston University) for communicating his quantum yield quenching data to us prior to publication.

Table 1. Variation of Products from the Photoreaction of Biacetyl and Tetramethylethylene under Various Conditions.[a]

Reactant	Solvent	Temperature	Percent (normalized/products) 1	2	3	4	%[b] Conversion	Type A/Type B
$(CH_3)_2C{=}C(CH_3)_2$	CH_3CN	ambient	56	35	3	6	41	10
$(CD_3)_2C{=}C(CD_3)_2$	CH_3CN	ambient	35	61	2	3	29	22
$(CH_3)_2C{=}C(CH_3)_2$	CH_3CN	-20°C	58	37	2	3	-	21
$(CH_3)_2C{=}C(CH_3)_2$	C_6H_6	ambient	41	22	15	22	70	1.7
$(CD_3)_2C{=}C(CD_3)_2$	C_6H_6	ambient	34	54	5	7	40	7.2
$(CH_3)_2C{=}C(CH_3)_2$	$n\text{-}C_6H_{14}$	ambient	33	3	23	41	46	0.6
$(CD_3)_2C{=}C(CD_3)_2$	$n\text{-}C_6H_{14}$	ambient	42	10	25	24	28	1.1
$(CH_3)_2C{=}C(CH_3)_2$	$n\text{-}C_6H_{14}$	-78°C	74	10	7	9	-	5.2

(a) Initial concentration of BA = TME = 0.1 M in CH_3CN, $n\text{-}C_6H_{14}$ and C_6H_6.

(b) % Conversion is based on the loss of BA and is for comparable doses, i.e., the ratio of conversion is equal to the ratio of quantum yields for net reaction.

Table 2. Kinetic Measurements of the Quenching of Biacetyl Phosphorescence at Ambient Temperature.[a]

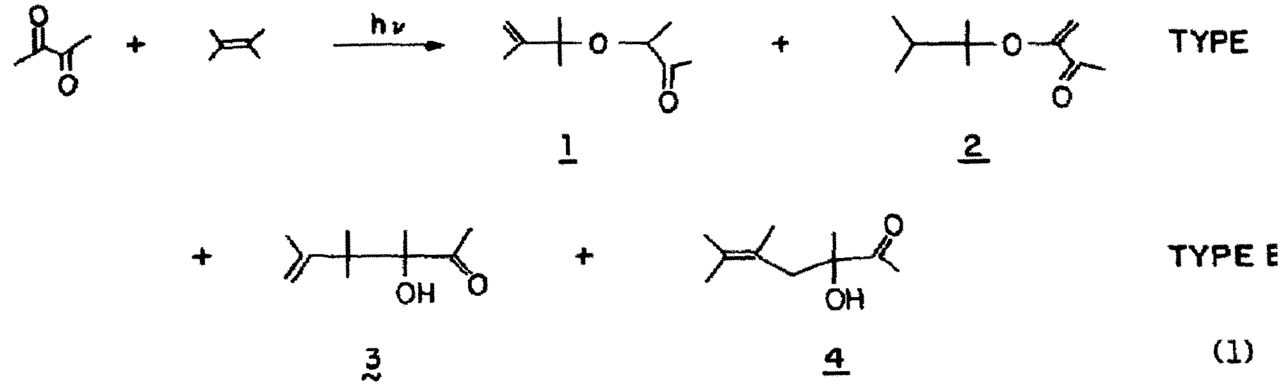
Quencher	Solvent	$k_q\tau$ (M^{-1})	k_q $(M^{-1}\ S^{-1})$
$(CH_3)_2C{=}C(CH_3)_2$	CH_3CN	1020[b]	7.0×10^6
$(CD_3)_2C{=}C(CD_3)_2$	CH_3CN	965[b]	6.6×10^6
$(CH_3)_2C{=}C(CH_3)_2$	$n\text{-}C_6H_{14}$	97[c]	2.8×10^5
$(CD_3)_2C{=}C(CD_3)_2$	$n\text{-}C_6H_{14}$	54[c]	1.5×10^5
$(CH_3)_2C{=}C(CH_3)_2$	C_6H_6	60[d]	4.5×10^5
$(CD_3)_2C{=}C(CD_3)_2$	C_6H_6	48[d]	3.6×10^5

(a) Concentration of BA = 0.04 M, TME = $5 \times 10^{-2} \sim 5 \times 10^{-3}$ M in C_6H_6, CH_3CN or $n\text{-}C_6H_{14}$, but TME = $5 \times 10^{-4} \sim 1 \times 10^{-2}$ M. Solutions deoxygenate by Ar bubbling.

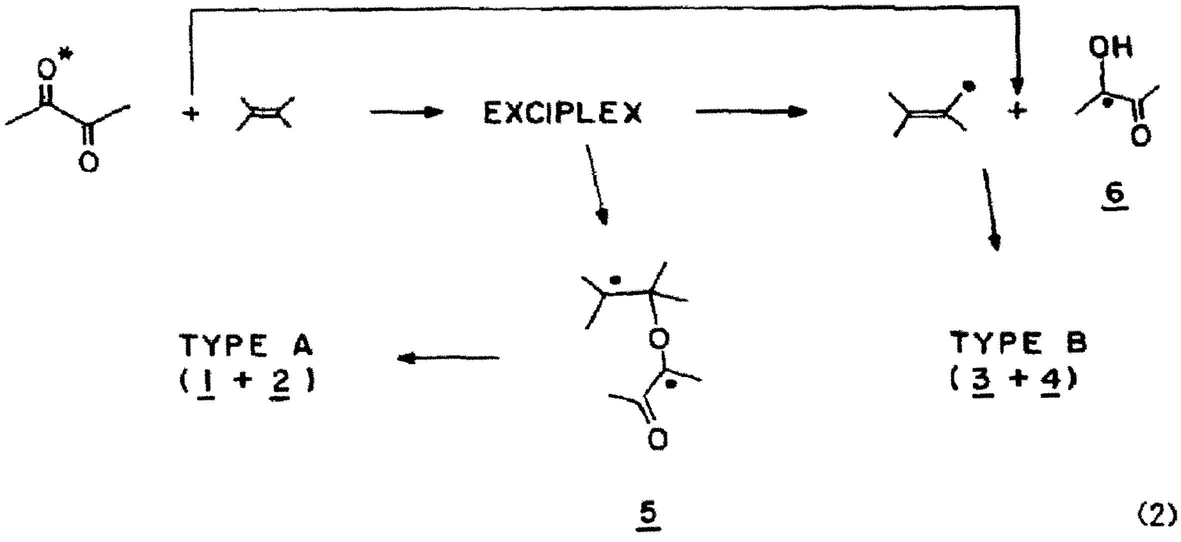
(b) τ_p in CH_3CN without quencher is 145 μs.

(c) τ_p in $n\text{-}C_6H_{14}$ without quencher is 336 μs.

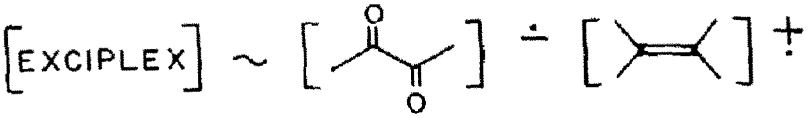
(d) τ_p in C_6H_6 without quencher is 135 μs.



(1)



(2)



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