of lyate species, decomposition of carbanion intermediate is *not dependent upon the concentration of any buffer species.* The only mechanism which we can envision which involves breakdown of carbanion to products and which does not depend upon any acid or base species present is an E1cB mechanism passing through intermediate ketene.[9]

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Received June 24, 1968

Secondary Deuterium Isotope Effects on the Transfer of Triplet Electronic Excitation to an Olefin

Sir:

The transfer of triplet electronic excitation from one molecule to another has been shown in recent years to be a common, and most useful, phenomenon in photochemistry.[1] The sequence of events is clearly the diffusion together of a triplet donor (or sensitizer) molecule and an acceptor (or substrate) molecule followed by an interaction between the two molecules which can result in excitation transfer. An obvious question which must be answered is: what is the nature of this interaction? Recently, Yang and coworkers[2] have proposed a mechanism for energy transfer from n–π* triplets of carbonyl compounds as donors to simple olefins as acceptors which involves intermediate A below. We wish at this time to report in preliminary form some of our results which illustrate that secondary
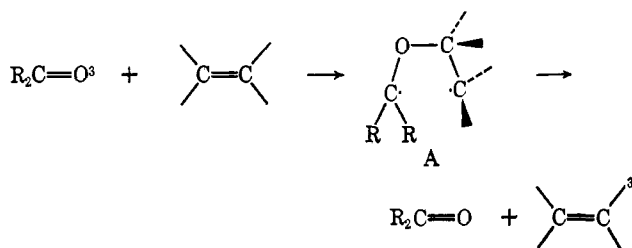
deuterium isotope effects can be useful mechanistic probes in studying energy-transfer mechanisms and caution that the scheme above is not general for the interaction between n–π* sensitizers and olefins.

We have prepared β-methylstyrene-β-d by the method of Schlosser[3] and have determined the secondary deuterium isotope effect on the photosensitized *trans–cis* isomerization. Samples of pure *trans*, about 50% labeled, were subjected to partial photosensitized isomerization to *cis* (<17%). The *trans* and *cis* isomers were isolated by preparative vpc and compared for deuterium content with the starting *trans* by mass spectrometry (Table I). Appropriate control experiments ensured that the work-up did not cause significant isotopic partitioning. Irradiations were performed on outgassed benzene solutions at

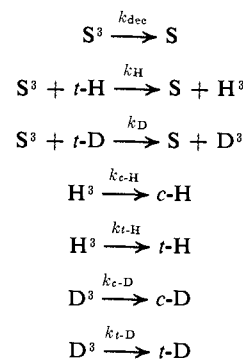(1) P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, 5, 21 (1968), and references therein.
(2) N. C. Yang, J. T. Cohen, and A. Shani, *J. Am. Chem. Soc.*, 90, 3264 (1968).
(3) M. Schlosser, *Chem. Ber.*, 97, 3219 (1964).

3660 Å. Quantum yields were measured using potassium ferrioxalate.

The most significant result is that *the initially produced cis is richer in the unlabeled compound than is the starting material.* Clearly there is an isotope effect in the "normal" direction, $k_H/k_D > 1$, on the photosensitized isomerization. We have not yet attempted to correct our results for either the change in isotopic content of the starting material during the isomerization or for the reverse isomerization that is occurring. Since the conversion is in all cases small, however, <20% to photostationary state, we expect that such corrections will be small.

We presume the mechanism below is operating. Here k_H and k_D refer to the rates of energy transfer from sensitizer to *trans*-β-methylstyrene (t-H) and *trans*-β-methylstyrene-β-d (t-D), respectively. The last four equations refer to decay of undeuterated triplet (H^3) and deuterated triplet (D^3) to *cis* and *trans* olefin.

$$S^3 \xrightarrow{k_{dec}} S$$

$$S^3 + t\text{-H} \xrightarrow{k_H} S + H^3$$

$$S^3 + t\text{-D} \xrightarrow{k_D} S + D^3$$

$$H^3 \xrightarrow{k_{c\text{-H}}} c\text{-H}$$

$$H^3 \xrightarrow{k_{t\text{-H}}} t\text{-H}$$

$$D^3 \xrightarrow{k_{c\text{-D}}} c\text{-D}$$

$$D^3 \xrightarrow{k_{t\text{-D}}} t\text{-D}$$

It may be easily shown that, for small conversion to *cis*

$$\frac{(c\text{-H})}{(c\text{-D})} \frac{\langle t\text{-D} \rangle}{\langle t\text{-H} \rangle} = \frac{k_H}{k_D} \frac{f_c^H}{f_c^D} \tag{1}$$

where f_c^H and f_c^D represent the fractions of undeuterated and deuterated triplets that decay to *cis*. The right-hand side is thus 1.15 ± 0.03 for fluorenone as a sensitizer and 1.15 ± 0.02 for biacetyl.

Complete dissection of the data into isotope effects on the energy-transfer step and on the triplet decay ratio must await further work. However, we feel that the contribution of the f_c term is probably small since: (a) no isotope effect was detected on the photostationary state reached with benzophenone (though, however, the error limits are large) and (b) there appears to be no deuterium isotope effect on the decay ratio of the stilbene triplet.[4]

Yang's[2] mechanism for energy transfer from n–π* ketone sensitizers predicts an isotope effect for biacetyl in the opposite direction to that we observe. It is well known that reactions involving a change of hybridization at carbon from sp² to sp³ show an inverse α deuterium isotope effect,[5] $k_H/k_D < 1$, and there is a ready explanation for this fact.[6] Though fluorenone is considered to have a π–π* lowest triplet,[7] biacetyl is

(4) J. Saltiel, *J. Am. Chem. Soc.*, 89, 1036 (1967).
(5) Some selected examples of inverse deuterium isotope effects in addition to olefins are: D. B. Denney and N. Tunkel, *Chem. Ind.* (London), 1383 (1959); M. Matsuoka and M. Szwarc, *J. Am. Chem. Soc.*, 83, 1261 (1961); S. Seltzer, *ibid.*, 83, 1861 (1961); T. J. Katz and R. Dessau, *ibid.*, 85, 2173 (1963).
(6) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *ibid.*, 80, 2326 (1958).
(7) K. Yoshihara and D. R. Kearns, *J. Chem. Phys.*, 45, 1991 (1966).

Table I. Photosensitized isomerization of

$$\underset{Ph \quad H(D)}{\overset{H \quad CH_3}{>\!=\!<}}$$

Sensitizer (E_T)	Starting isomer (D/H)[a]	% convn	D/H[a] (recovered *trans*)	D/H[a] (*cis*)	$\phi_{t\rightarrow c}$[b]	$\phi_{c\rightarrow t}$[b]	% cis at photostationary state
Fluorenone (53.3)	*trans* (1.050 ± 0.003)	16.9	1.08 ± 0.02	0.91 ± 0.01	0.38 (0.5 M)		78[e]
		8.7	1.05 ± 0.005	0.93 ± 0.007	0.40 (0.5 M)		
Biacetyl (54.9)	*trans* (0.966 ± 0.005)	10.3	0.980 ± 0.008	0.85 ± 0.01	0.42	>0.39[f]	88[e,g]
Thioxanthone (65.5)					0.45	0.50	
Benzophenone (68.5)	*cis* (1.07 ± 0.02)	64[d]	1.06 ± 0.05	1.06 ± 0.06	0.51[c]	0.51[c]	65[c]
Propiophenone (74.6)					0.44	0.50	55[e]

[a] The ratio of m/e 119 to m/e 118, corrected for ^{13}C contribution to the m/e 119 peak. The precision represents the 95% confidence level for the mean of ten scans. [b] Quantum yields uncorrected for back-reaction, measured at about 5% conversion in solutions 0.05 M in β-methylstyrene, except as noted. [c] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965). [d] Photostationary state. [e] At 0.06 M. Recovery of material was essentially quantitative for fluorenone, but in the region of 30–60% in other cases at photostationary state. [f] The photostationary state is so rich in *cis* isomer that back-reaction correction to this number is significant even at 5% conversion. It is accordingly a minimum value for the initial $\phi_{t\rightarrow c}$. [g] This number may be sensitive to the extent of decomposition of the sample.

clearly n–π*.[8] Addition of a biacetyl triplet to β-methylstyrene should occur in the β (labeled) position if Yang's[2] mechanism were operating, since only that mode of addition permits delocalization of an odd electron into the benzene ring. Consequently, an inverse deuterium isotope effect would be expected, contrary to our observation. It is possible that the isomerizations observed by Yang[2] did not involve free olefin triplets at all. We feel that our experiments probably do, since the constancy of $\phi_{t\rightarrow c}/\phi_{ic}$ at 0.43 ± 0.02 for all our data is readily interpretable on the basis that f_c of eq 1 = 0.43 (or slightly higher, since the back-reaction correction was not made).

The interpretation of the result that $k_H/k_D > 1$ must remain somewhat speculative until more is known about the details of energy-transfer mechanisms. Schmidt and Lee[9] have recently reported similar observations with benzene and acetone triplets as donors and C_2H_4 or C_2D_4 as quencher. Their explanation is based on the observation of Evans[10] that deuteration shifts the apparent onset of singlet–triplet absorption in ethylene to higher energies. Should it turn out that Evans' results relate to the true triplet energies (0–0 bands) of C_2H_4 and C_2D_4 *and* that energy transfer is in any of these cases a process involving the spectroscopic olefin triplet, then it would be expected that k_H/k_D would be greater than 1.

On the other hand, Hammond[11] has investigated "endothermic" triplet energy transfer and has presented results which strongly suggest that the donor–acceptor interaction can involve nonspectroscopic states of the acceptor. Simple olefin triplets are expected to have energy minima at geometries in which considerable twist around the double bond has occurred.[12] We consider it likely that relatively low-energy "twisted"

states are available for β-methylstyrene. They may well be involved in these "endothermic" energy transfers (the triplet energy for *trans*-β-methylstyrene has been determined to be 59.8 kcal/mol[13]).

We believe an isotope effect in the observed direction can be rationalized equally well if spectroscopically inaccessible states of the acceptor are involved. The energy-transfer probability would be expected to depend upon Franck–Condon factors.[14] We feel there is reason to expect them to be larger when the substrate is undeuterated, and therefore to expect $k_H/k_D > 1$. The line of reasoning would be somewhat analogous to that conventionally used to explain the deuterium isotope effects, $k_H/k_D > 1$, on radiationless decay rates of triplet-state organic molecules.[15]

Much further work is needed to determine rate constants, temperature effects, and isotope effects in a variety of systems before very detailed understanding of endothermic energy transfer from organic sensitizer triplets will emerge.

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(11) (a) J. Saltiel and G. S. Hammond, *J. Am. Chem. Soc.*, **85**, 2515 (1963); (b) G. S. Hammond and J. Saltiel, *ibid.*, **85**, 2516 (1963); (c) G. S. Hammond, *et al.*, *ibid.*, **86**, 3197 (1964); (d) W. G. Herkstroeter and G. S. Hammond, *ibid.*, **88**, 4769 (1966).
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A Novel Synthesis of Isomerically Pure α,β-Unsaturated Nitriles *via* Hydroalumination of Alkynes[1]

Sir:

The facile reactions of vinylalanates with carbon dioxide and halogens, which provide stereoselective