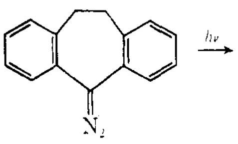
photolysis, all of them were obtained in the gas phase.

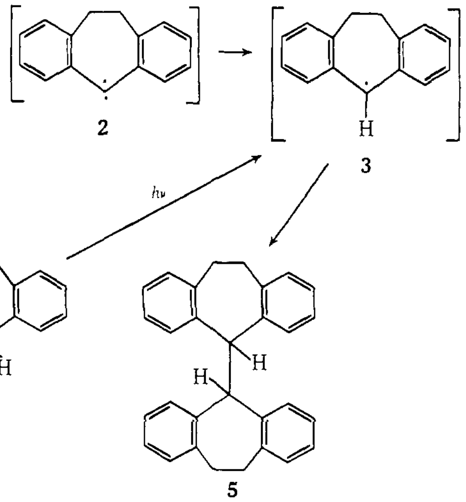
We wish to report here that we have obtained, for the first time, the electronic absorption spectrum of 10,11-dihydrodibenzo[*a,d*]cycloheptenylidene (**2**) by the flash photolysis of 5-diazo-10,11-dihydrodibenzo[*a,d*]-cycloheptadiene (**1**)[11] *in liquid paraffin at room temperature*.

The flash photolysis of a *ca.* 5.3×10^{-5} *M* solution of **1** in deoxygenated paraffin at room temperature was studied using the apparatus previously described.[12] The change in the transient spectra was investigated with various delay times in the range from 1 μsec to 1 sec. The absorption spectrum appearing at the delay time of 5 μsec is shown by curve C in Figure 1. The spectrum of the intermediate changed with time and took the shape as shown by curve D at the delay time of 450 μsec, and then disappeared within 25 msec. The lifetime of the former intermediate is estimated to be in the range of about 1–50 μsec.

The spectral feature of curve C agrees well with the spectrum of carbene **2** previously observed in the rigid media at 77°K (curve A), and therefore it may be reasonable to conclude that the same carbene is formed in the liquid paraffin by the flash photolysis. The spectral characteristics of curve D are very similar to those obtained by the flash photolysis of the solution of 10,11-dihydrodibenzo[*a,d*]cycloheptene (**4**) and the photolysis product of **4** in rigid media (curve B) and therefore may safely be assigned to the radical **3**.[13]



1



2

3

4

5

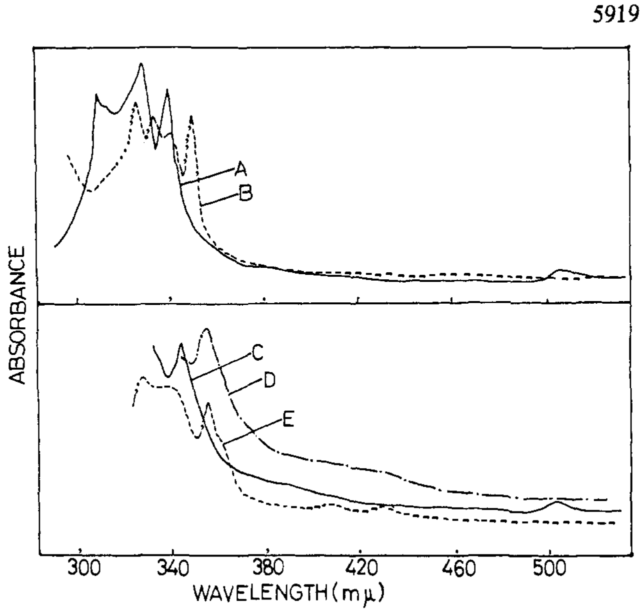


Figure 1. Electronic absorption spectra of 10,11-dihydrodibenzo-[*a,d*]cycloheptenylidene and 10,11-dihydrodibenzo[*a,d*]cycloheptenyl radical: (A) absorption spectrum of carbene **2** produced by photolysis of **1** at 77°K with a Hg lamp; (B) absorption spectrum of radical **3** produced by photolysis of **4** at 77°K with a Hg lamp; (C) absorption spectrum of carbene **2** produced by flash photolysis of **1** at 20° at the delay time of 5 μsec; (D) the same as (C) taken at the delay time of 450 μsec; (E) absorption spectrum of radical **3** produced by flash photolysis of **4** at 20°.

From these results, it seems reasonable to conclude that radical **3** is formed as a result of the hydrogen abstraction by the carbene **2** from the solvent. Analysis of the ultimate products has established that the principal product is 5,5′-bi(10,11-dihydrodibenzo[*a,d*]cycloheptenyl) (**5**) presumably formed by the dimerization of radical **3**. The absorption spectrum of **5** is of course quite different from the transient spectra obtained. When the flash photolysis was carried out in a liquid paraffin solution containing oxygen, spectrum C did not appear and a new transient spectrum with a maximum at 450 mμ was obtained.

In view of the fact that the T–T′ absorption spectrum of carbene **2** can be observed in solution at room temperature at the delay time of 3 μsec, it seems reasonable to assume that the singlet–triplet intersystem crossing may occur within *ca.* 1 μsec at room temperature.

---

(9) G. Herzberg and J. Shoosmith, *Nature*, **183**, 1801 (1959); G. Herzberg, *Proc. Roy. Soc.* (London), **A262**, 291 (1961); G. Herzberg, *Can. J. Phys.*, **39**, 511 (1961).

(10) (a) P. Venkateswarlu, *Phys. Rev.*, 77, 79, 676 (1950); P. K. Laird, E. B. Andrews, and R. F. Barrow, *Trans. Faraday Soc.*, **46**, 803 (1950); D. E. Mann and B. A. Thrush, *J. Chem. Phys.*, **33**, 1732 (1960); B. A. Thrush and J. J. Zwolenik, *Trans. Faraday Soc.*, **59**, 582 (1963); R. E. Milligan, D. E. Mann, M. E. Jusk, and R. A. Mitsch, *J. Chem. Phys.*, **41**, 1199 (1964); J. P. Simons, *J. Chem. Soc.*, 5406 (1965); (b) A. J. Merer and D. N. Travis, *Can. J. Phys.*, **39**, 511 (1961); (c) A. J. Merer and D. N. Travis, *ibid.*, **44**, 1541 (1966); (d) *ibid.*, **44**, 525 (1966).

(11) I. Moritani, S. Murahashi, K. Yoshinaga, and H. Ashitaka, *Bull. Chem. Soc. Japan*, **40**, 1506 (1967).

(12) N. Yamamoto, Y. Nakato, and H. Tsubomura, *ibid.*, **39**, 2603 (1966).

(13) The slight differences in the wavelengths of the absorption maxima, and the broadness of the bands, *e.g.*, between A and C in Figure 1, may be attributed to the differences in temperature and solvents. Although there are some other minute disagreements in the spectra of these unstable species, we have reached the conclusion given above in view of the general characteristics of these spectra.

Ichiro Moritani, Shun-Ichi Murahashi, Hidetomo Ashitaka
Katsumi Kimura, Hiroshi Tsubomura
Department of Chemistry, Faculty of Engineering Science
Osaka University, Machikaneyama, Toyonaka, Osaka, Japan

Received July 3, 1968

Deuterium Isotope Effect in Triplet Electronic Energy Transfer Rates. From Benzene and Acetone to Olefins

Sir:

We wish to report a preliminary account of a study of the deuterium rate isotope effect observed in the triplet excitation energy transfer process in the gas

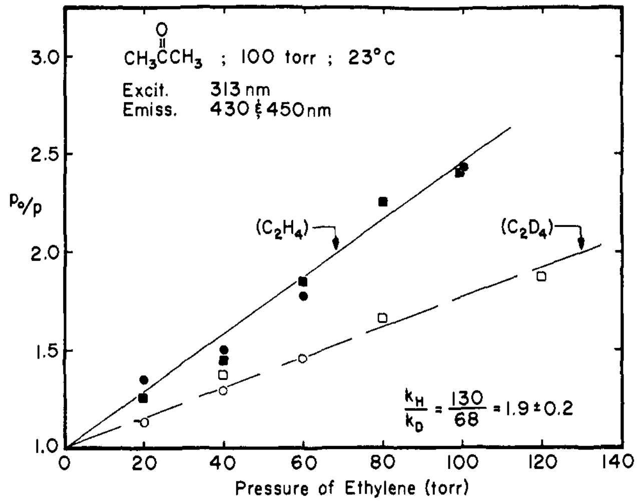


Figure 1. Quenching of the acetone phosphorescence by addition of C_2H_4 and C_2D_4.

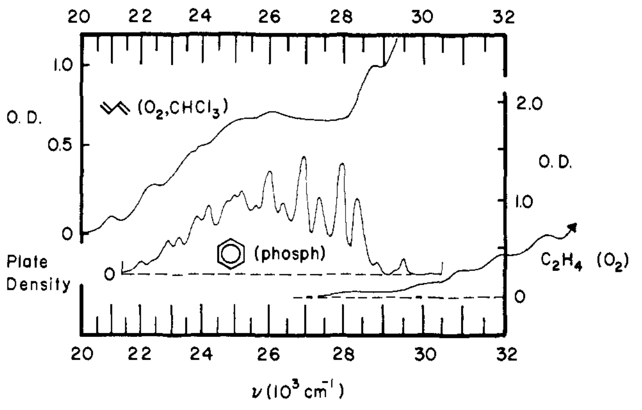


Figure 2. Absorption and emission profiles. For O_2 perturbation see ref 3a; for C_6H_6 phosphorescence see ref 9.

phase. It is represented by $^3D + A \rightarrow D + A^*$, where ^3D is the triplet donor molecule (benzene or acetone in its lowest triplet state) and A is the olefinic quencher molecule (ethylene and propylene in its ground electronic state). Earlier studies have shown that, for example, the collisional efficiencies of C_2H_4 and 1,3-butadiene in quenching the triplet C_6H_6 ($E_T = 84$ kcal/mole) are $\sim$0.01 and $\sim$0.5, respectively,[1] while the efficiencies in quenching the triplet acetone ($E_T \approx 78$ kcal/mole) are 5×10^{-6} and 0.03, respectively.[2] Since it is believed that the 0,0 bands of the lowest triplet C_2H_4 and 1,3-butadiene are located at $\leqslant 82$[3] and 60 kcal/mole,[3,4] respectively, it was suggested that the quenching efficiency increases with the decreasing endothermicity[2] (or possibly with the increasing exothermicity[1]) of the spin-exchange process. However, the mechanistic details for generating such a rate–energetics correlation are not known.

The present experimental measurements involve monitoring of either the competitive quenching of benzene-photosensitized *cis–trans* isomerization of 2-butenes by olefinic quenchers or the quenching of acetone phosphorescence emission at room temperature and pressures identical with those employed earlier.[1,2,5] Observation a disclosed that the acceptor isotope effect on quenching rate constants (k_H of C_2H_4/k_D of C_2D_4) for the triplet C_6H_6 is 1.7 ± 0.2, while the corresponding ratio for the triplet CH_3COCH_3 is 1.9 ± 0.2, as shown in Figure 1. A somewhat lower deuterium rate isotope effect, however, is found with propylene as a quencher.

Evans has suggested that the onset of the O_2-induced singlet–triplet absorption of C_2H_4 at 28,700 cm^{-1} and that of C_2D_4 at 28,940 cm^{-1} (observation b) are likely to be close to the 0,0 bands if they were not the 0,0 bands,[3a] and thus the threshold for the S → T excitation of C_2D_4 may be about 0.7 kcal/mole higher than that of C_2H_4. Therefore, on energetic grounds, it is reasonable to expect the diminution of the triplet energy transfer rate upon the deuterium substitution in ethylene, if the process involving C_2H_4 and the triplet donor requires an activation energy.

Rebbert and Ausloos observed that the phosphorescence quenching constant of propylene (and tetramethylethylene) for the triplet CD_3COCD_3 was 1.14 times greater than that for the triplet CH_3COCH_3.[2] The phosphorescence lifetime ($\tau^H{}_p$) of CH_3COCH_3 in the presence of mercury (25°, 30 torr) has been measured to be 0.18 msec,[6] while $\tau^H{}_p$ of CH_3COCH_3 and $\tau^D{}_p$ of CD_3COCD_3 in the mercury-free system are known to be 0.20 and 0.51 msec at 25° and 100 torr.[7] Combining the above sets of experimental data (observation c),[2,6,7] one obtains the donor isotope effect on the quenching rate constants (k_H' for CH_3COCH_3/k_D' for CD_3COCD_3) of $(0.51/0.20) \div 1.14 = 2.2$ when nondeuterated propylene (or tetramethylethylene) is used as an acceptor. This donor isotope effect is clearly complementary to the acceptor isotope effect discussed above.

A comparison of the O_2-perturbed singlet → triplet transition profiles of C_2H_4, C_2D_4, and 1,3-butadiene measured by Evans[8] with the triplet → singlet transition profile of C_6H_6[9] indicates that the excitation curve of C_2H_4 overlaps poorly with the benzene phosphorescence curve, the excitation curve of C_2D_4 overlaps even more poorly than C_2H_4 near its absorption edge, and the overlap between 1,3-butadiene and benzene is very favorable (observation d; Figure 2). Therefore, the high degree of overlap parallels the high degree of collisional efficiency in the triplet energy transfer between benzene and olefins. A similar criterion can be applied

---

(1) (a) G. A. Haninger, Jr., and E. K. C. Lee, *J. Phys. Chem.*, **71**, 3104 (1967); (b) E. K. C. Lee, H. O. Denschlag, and G. A. Haninger, Jr., *J. Chem. Phys.*, **48**, 4547 (1968).

(2) R. E. Rebbert and P. Ausloos, *J. Am. Chem. Soc.*, **87**, 5569 (1965).

(3) (a) D. F. Evans, *J. Chem. Soc.*, 1735 (1960). The absorption maximum at 2700 Å in the O_2-induced spectra for C_2H_4 corresponds to the S → T transition to the Franck–Condon state. (b) R. S. Mulliken, *J. Chem. Phys.*, **33**, 1597 (1960). (c) A. Kuppermann and L. M. Raff, *Discuss. Faraday Soc.*, **35**, 30 (1963).

(4) R. E. Kellogg and W. T. Simpson, *J. Am. Chem. Soc.*, **87**, 4230 (1965).

(5) R. B. Cundall, F. J. Fletcher, and D. G. Milne, *Trans. Faraday Soc.*, **60**, 1146 (1964).

(6) W. E. Kaskan and A. B. F. Duncan, *J. Chem. Phys.*, **18**, 427 (1950).

(7) A. Gandini, D. A. Whytock, and K. O. Kutschke, *Ber. Bunsenges. Phys. Chem.*, **72**, 296 (1968). A considerably smaller value of $\tau^D{}_p/\tau^H{}_p = 1.3$ may be estimated from the reported value of $\Phi^D{}_p/\Phi^H{}_p = 1.3$,[2] if $\Phi^D{}_{S\rightarrow T} = \Phi^H{}_{S\rightarrow T} = 1.00$ in the gas phase can be *safely assumed while no such direct measurements exist* (see A. S. Davies and R. B. Cundall, *Progr. Reaction Kinetics*, **4**, 149 (1967). Thus, we prefer the use of the *directly measured values* of GWK.

(8) See ref 3a. The optical densities were recorded for these molecules, and a semiquantitative estimate of the relative radiative transition probabilities can be made.

(9) See, for example, the phosphorescence emission spectra (in EPA) obtained at 77°K by H. Shull, *J. Chem. Phys.*, **17**, 295 (1949).

in the triplet energy transfers between acetone and olefins. Now, an assignment of about 1 kcal/mole lower triplet energy (E_T) per alkyl substituent in ethylene appears reasonable,[10,11] since observations a and b indicate that an energy difference of 0.7 kcal/mole for E_T's in C_2H_4 and C_2D_4 introduces an energy transfer rate ratio of about 1.8.

Several conclusions follow: (1) observations a and b indicate that the acceptor excitation process in the triplet energy transfer and the O_2-induced S → T absorption process are alike with regard to the observed deuterium isotope effects; (2) observations a and c strongly suggest that the rate-determining factors in the appropriate combinations of radiationless transitions during the collisional encounter of the donor and the acceptor are largely *intramolecular* in nature,[12] and they suggest further that the lifetime variation of the donor–acceptor collision pair is not likely to be important in governing the variations of the relative quenching efficiencies (for a given donor); (3) observation d implies that the chief rate-controlling factor for the energetically unfavorable collisional energy-transfer processes is the extent of the overlap between the deexcitation function of the donor and the excitation function of the acceptor (radiative as well as radiationless transition probability *vs.* energy); and (4) the reason for the lack of large deuterium rate isotope and alkyl substitution effects in quenching the $Hg(^3P_1)$ atom by olefins[13] lies in the fact that this triplet energy transfer process is favorably exothermic and that the deuterium isotope effect is more pronounced at the transition thresholds.[14,15]

We believe that the measurement of the deuterium rate isotope effect is useful as a probe in the study of the intermolecular electronic energy-transfer processes, as has been demonstrated in the study of the Franck–Condon factors and the *intramolecular* relaxation processes.[16,17] Further study on the donor isotope effect will be useful in establishing the mechanism in greater detail.

Acknowledgment. This research has been supported by a National Science Foundation grant (GP 6924). Helpful discussions with Professor Max Wolfsberg early in the investigation are greatly appreciated.

[10] Each alkyl substituent in ethylene raises the efficiency of quenching of the triplet donors by a factor of 2 (see ref 1 and 2).

[11] Analogous rate–energy correlations for a variety of the donor–acceptor pairs have been observed in the condensed phase studies: (a) G. Porter and F. Wilkinson, *Proc. Roy. Soc.* (London), **A164**, 1 (1961); (b) K. Sandros and H. L. J. Backstrom, *Acta Chem. Scand.*, **16**, 958 (1962); (c) W. G. Herkstroeder and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4769 (1966).

[12] See for example the discussion of the isotope effect observed in the phosphorescence lifetimes of acetone-d_6 and acetone-h_6 in the frozen medium by R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966); acetone-d_6 has a much longer intramolecular relaxation time than acetone-h_6.

[13] (a) H. E. Gunning and O. P. Strausz, *Advan. Photochem.*, **1**, 209 (1963); (b) R. J. Cvetanović, *Progr. Reaction Kinetics*, **2**, 39 (1964).

[14] A. A. Gordus and R. B. Bernstein, *J. Chem. Phys.*, **22**, 790 (1954).

[15] It is observed that k_H/k_D for the pair 1,3-butadiene and 1,3-butadiene-d_6 in quenching the triplet C_6H_6 is 1.0 ± 0.2 while k_H/k_D in quenching the triplet biacetyl (E_T = 57 kcal/mole) is 2.0 ± 0.3. The details of this study will soon be published.

[16] G. W. Robinson, *J. Mol. Spectry.*, **6**, 58 (1961).

[17] W. Siebrand and D. F. Williams, *J. Chem. Phys.*, **46**, 403 (1967).

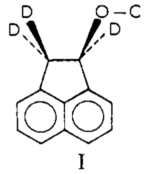
Manfred W. Schmidt, Edward K. C. Lee
Department of Chemistry, University of California
Irvine, California 92664

Received June 10, 1968

Effect of Cation on the Stereochemistry of Hydrogen–Deuterium Exchange

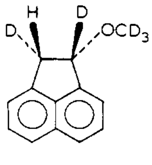
Sir:

We have observed an inversion in the stereochemistry of base-catalyzed hydrogen–deuterium exchange dependent only on the nature of the cations present in solution. The rigid system, 1-trideuteriomethoxy-1,2,2-trideuterioacenaphthene (I), was prepared and the deuterons were exchanged in *t*-butyl alcohol. The base varied from lithium *t*-butoxide through the potassium to tetramethylammonium salts.

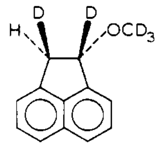


I

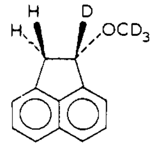
Experimentally the substrate (0.04–0.16 *M*) was treated in sealed, degassed tubes under the conditions reported in Table I. Concurrent with an elimination reaction producing acenaphthylene, exclusive exchange at the 2 positions was observed. Thus the products of exchange are *cis*-h_1, *trans*-h_1, and h_2 as designated below.



trans-h_1



cis-h_1



h_2

The olefin–ether mixture was analyzed by vpc and the mixture separated by elution chromatography. The exchanged ether was distilled (>80% recovery) and analyzed by nmr (15 wt % in CCl_4) for relative amounts of protons *cis* and *trans* to the OCD_3 group.[1] Isotopic analysis by mass spectrometry (Varian M-66) determined the relative amounts of d_6, d_5, and d_4 material. Combination of both pieces of information allows an estimate of the amounts of I, *cis*-h_1, *trans*-h_1, h_2, and acenaphthylene as reported in Table I.

The results of run 1 of Table I with tetramethylammonium *t*-butoxide as base show preferential hydrogen incorporation *trans* to the methoxyl group (*i.e.*, more *trans*-h_1 than *cis*-h_1). Runs 2 and 3 with potassium *t*-butoxide show just the opposite behavior with hydrogen incorporation occurring predominantly *cis* to the methoxyl group. With lithium *t*-butoxide, runs 4 and 5, exchange occurred exclusively *cis* to the methoxyl group. These changes are demonstrated more clearly by converting the data of Table I into the k^{cis}/k^{trans} ratios reported in Table II.

The rate ratio has changed by at least a factor of 45 depending on the nature of the cation with the exchange preference crossing from predominantly *trans* to exclusively *cis*. Although the calculated ratio, k^{cis}/k^{trans}, will depend upon the elimination reaction, preliminary results indicate that the actual ratio for lithium would

---

[1] Stereochemical assignments are based upon coupling constants obtained from an ABX analysis of the spectrum of 1-trideuteriomethoxyacenaphthene (δ_{cis} 3.11 ppm, δ_{trans} 3.32 ppm, δ_X 5.06 ppm, $J_{cis,trans}$ = 17.2 Hz, $J_{cis,X}$ = 2.7 Hz, $J_{trans,X}$ = 6.9 Hz) and upon the agreement of these coupling constants and relative chemical shifts with about 20 1-substituted acenaphthenes (S. Sternhell, private communication).