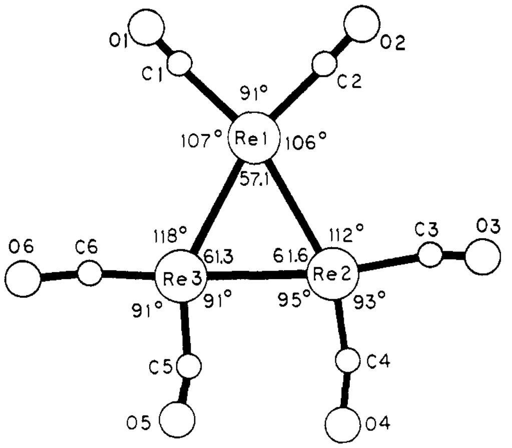
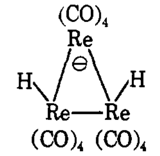
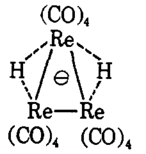


Figure 2. Angles around the equatorial carbonyl ligands in the $[H_2Re_3(CO)_{12}^-]$ ion.

the spectroscopic data (*vide infra*) are clearly not in agreement with this.



A



B

In acetone solution four principal absorptions were observed in the carbonyl stretching region of the infrared: 2053 m, 2008 vs, 1949 m, and 1897 m cm^{-1} (Beckman IR-4, LiF prism). A fifth very weak absorption was observed at 2105 cm^{-1} which corresponds to the most intense carbonyl band in the Raman spectrum (Cary Model 81, Laser Raman). With appropriate shift to lower energy on account of the negative charge, the pattern of four principal infrared bands largely resembles that of the parent compound $H_3Re_3(CO)_{12}$[2] (2093 m, 2030 vs, 2008 s, 1983 m cm^{-1}). It would appear that only a small perturbation from D_{3h} symmetry of the neutral species has occurred in the anion; structure A of C_{2v} symmetry would require up to ten CO absorptions in the infrared. The apparent high symmetry inferred from the infrared bands denotes extensive delocalization of the negative charge and corresponding shift of hydrogen atoms, structure B.

A sample of $[(C_6H_5)_4As^+]$ $[D_2Re_3(CO)_{12}^-]$ was prepared from $D_3Re_3(CO)_{12}$,[6] and its infrared and Raman spectra were compared with those of I. No bands characteristic of a terminal Re-H (*ca.* 1800–2200 cm^{-1}) or a terminal Re-D (*ca.* 1250–1550 cm^{-1}) were observed. On the other hand, we did observe absorptions near 1100 cm^{-1} in the Raman spectrum of the Re-H derivative which changed or disappeared in the spectrum of the Re-D derivative while new bands appeared near 800 cm^{-1}. From work on other metal hydride complexes,[7] we have come to associate such features with metal-hydrogen in the bridging environment shown in structure B and Figure 1.

If one assumes that the hydride ligands are approximately *trans* to C(1)O(1) and C(4)O(4), and to C(2)O(2) and C(5)O(5), the Re-H distance may be estimated as ~1.7 Å, in good agreement with the value predicted from the Re-H-Re distance of 3.392 Å in $HRe_2Mn(CO)_{14}$.[3]

The yellow anion $H_2Re_3(CO)_{12}^-$ is also obtained by acidification of the red dianion $HRe_3(CO)_{12}^{2-}$ which has recently been isolated as the $(C_6H_5)_4As^+$ salt from the carbonyl metalate solutions derived from $Re_2(CO)_{10}$ and $NaBH_4$ and whose characterization and structure is presently also under investigation.

Acknowledgment. We are grateful to Dr. J. R. Holmes and Mr. S. Kirtley for assistance in obtaining the Raman spectra and for valuable discussions.

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Received September 3, 1968

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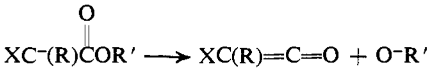
[6] J. M. Smith, K. Mehner, and H. D. Kaesz, *J. Am. Chem. Soc.*, **89**, 1759 (1967).

[7] (a) J. M. Smith, W. Fellmann, and L. H. Jones, *Inorg. Chem.*, **4**, 1361 (1965); (b) R. Bau and H. D. Kaesz, manuscript in preparation.

The Establishment of a Carbanion Mechanism for Ester Hydrolysis and the Unimportance of Electrostatic Effects of α Substituents on the Rates of Hydroxide Ion Attack at the Ester Carbonyl Group[1]

Sir:

Ionization of an α-H from esters of type XCH(R)-COOR′ to produce a carbanion has been suggested: (a) to *impede* alkaline hydrolysis of *p*-nitrophenyl acetate carbanion *via* electrostatic repulsion of the attacking hydroxyl ion,[2] and (b) to *enhance* ester hydrolysis[3] (or alcoholysis[4]) *via* an elimination reaction which would yield a highly reactive ketene intermediate (eq 1).[3] In addition it has been stated[5] that a negative charge on X decreases the rates of alkaline hydrolysis due to electrostatic shielding.



$$XC^-(R)\overset{\overset{\displaystyle O}{\|}}{C}OR' \longrightarrow XC(R){=}C{=}O + O^-R' \qquad (1)$$

Results obtained in this laboratory when OR′ = *o*- or *p*-nitrophenolate (*o*-NP and *p*-NP, respectively) establish: (a) the first really compelling evidence for mechanism 1; (b) the experimental basis for the suggestion that electrostatic shielding by the carbanion of *p*-nitrophenyl acetate inhibits HO$^-$ attack is fallacious; and (c) electrostatic shielding or acceleration of HO$^-$ attack by negative or positive charges on X is kinetically unimportant.

The second-order rate constant for HO$^-$-catalyzed hydrolysis of *p*-nitrophenyl acetate (*p*-NPA) is invariant (882 l. mol^{-1} min^{-1}) in the range [HO$^-$] = 10^{-6} to 0.5 *M* (with KOH at 30 ± 0.1° in H_2O; μ = 1.0 with KCl). Thus, there is no evidence for an anionic species of *p*-NPA and the suggested[2] shielding of HO$^-$ attack by this species.

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[1] This work was supported by a grant from the National Institutes of Health.

[2] E. Sacher and K. J. Laidler, *Can. J. Chem.*, **42**, 2404 (1964).

[3] J. Casanova, Jr., N. D. Werner, and H. R. Kiefer, *J. Amer. Chem. Soc.*, **89**, 2411 (1967).

[4] W. A. Remers, R. H. Roth, and M. J. Weiss, *J. Org. Chem.*, 30, 2910 (1965).

[5] R. P. Bell and B. A. W. Coller, *Trans. Faraday Soc.*, **61**, 1445 (1965).

For esters of the type $XC(R_2)COO(o\text{-}NP)$ in which $XC(R_2) = Cl_2CH, C_5H_5N^+, CH_3, ClCH_2, BrCH_2, NCC(CH_3)_2, (CH_3)_3N^+CH_2, C_6H_5OCH_2, C_2H_5SCH_2, C_6H_5CH_2, CH_3CH_2$, and $CH_3CH_2CH_2$, the rate law for solvolysis is (2). A plot of log k_{OH} *vs.* log k_{H_2O} is found

$$k_{obsd} = k_{OH}[HO^-] + k_{H_2O}[H_2O] \qquad (2)$$

to be linear (eq 3) with little or no deviation of points corresponding to esters with formal positively charged X groups. Thus, the negative HO^- species is not

$$\log k_{OH} = 0.84 \log k_{H_2O} + 8.0 \qquad (3)$$

favored as a nucleophile over the neutral H_2O species by positively charged substituents. This result, when coupled with our previous findings for the hydrolysis of ethyl *o*-nitrophenyl oxalate and the monoanion of mono(*o*-nitrophenyl) oxalate,[6] establishes that electrostatic effects are unimportant under the conditions investigated (solvent H_2O, 1.0 *M* ionic strength with KCl, 30 ± 0.1°).

For the esters $XCH_2COO(o\text{-}$ or $p\text{-}NP)$, in which $X = COOC_2H_5$ or CN, log k_{obsd}–pH rate profiles for solvolysis are not derivable from (2) (Figure 1). For these esters the values of k_{H_2O} are as anticipated from the σ_I constants for X, but the term $k_{OH}[HO^-]$ of eq 2 must be replaced by an expression indicating a change from first- to zero-order dependence on $[HO^-]$ at certain pH values. In contrast, the hydrolysis of esters $NCC(CH_3)_2COO(o\text{-}$ or $p\text{-}NP)$ and $C_2H_5OOCC(CH_3)_2COO(o\text{-}$ or $p\text{-}NP)$, which possess no enolizable hydrogens, follows the rate law of (2). The change in the order of dependence on $[HO^-]$ with pH and the necessity to have enolizable hydrogens to observe this behavior are in accord with the formation of carbanions.[7] Carbanion formation when X = CN and $COOC_2H_5$ but not when X is any of the other functional groups listed above is in accord with the necessity for resonance stabilization. That the carbanion *occurs* along the reaction path and not *via* a nonproductive side equilibrium is supported by the fact that carbanion formation facilitates rather than impedes hydrolysis (*e.g.*, at pH ~7, the hydrolytic rates for the cyano and malonate esters are ~40 and ~10^4 greater, respectively, than predicted from eq 3). The log k_{obsd}–pH profiles for hydrolysis of the malonate and cyanoacetate esters are derivable from the mechanisms of (4).[8] For the

$$\begin{tikzcd} E \arrow[r, shift left, "k_1\Sigma B"] \arrow[rr, bend left, "k_{H_2O}[H_2O]"] & C \arrow[l, shift left, "k_2\Sigma BH"] \arrow[r, "k_3"] & \text{products} \end{tikzcd} \qquad (4)$$

ester $C_2H_5OOCCH_2COO(o\text{-}NP)$ (Figure 1) the log k_{obsd}–pH profile including all three plateau regions is

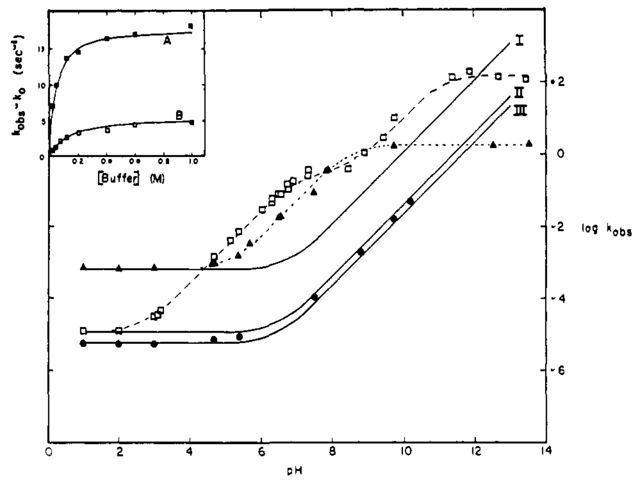

Figure 1. Solid lines I, II, and III are theoretical log k_{obsd}–pH profiles for the hydrolysis of $NCCH_2COO(o\text{-}NP)$, $EtOOCCH_2COO(o\text{-}NP)$, and $EtSCH_2COO(o\text{-}NP)$, respectively (as calculated from eq 3 employing the experimental value of k_{H_2O}). The experimental points (●) for the hydrolysis of $EtSCH_2COO(o\text{-}NP)$, a normal ester of general structure $XCH_2COO(o\text{-}NP)$, are seen to fit reasonably well the appropriate theoretical curve of III. For the α-cyanoacetate (▲) and malonate esters (□) the experimental points are as predicted for k_{H_2O} (from log k_{H_2O} *vs.* σ_I) but deviate greatly from the theoretical curves (I and II, respectively) in the alkaline pH range. The broken curves fitting the experimental points for the cyano and malonate esters were derived from eq 4. In the insert, total buffer concentration is plotted *vs.* the pseudo-first-order rate constant for the disappearance of $EtOOCCH_2COO(o\text{-}NP)$ at constant pH (A, morpholine at pH 8.69; B, tris(hydroxymethyl)aminomethane at pH 8.22). All experiments at 30 ± 0.1° and μ = 1.0 with KCl.

quantitatively fitted by (5). From (4), it is necessary

$$\begin{tikzcd} E \arrow[r, shift left, "\begin{matrix}6.5\times10^4[HO^-]\\0.32[H_2O]\end{matrix}"] \arrow[rr, bend right, swap, "2.25\times10^{-7}[H_2O]"] & C \arrow[l, shift left, "\begin{matrix}10^4[H_3O]\\4.0[H_2O]\end{matrix}"] \arrow[r, "10^2"] & \text{products} \end{tikzcd} \qquad (5)$$

to assume spontaneous breakdown of carbanion intermediates, and the only reasonable mechanism is one involving elimination of nitrophenoxide and production of ketene.

The reactions of $C_2H_5OOCCH_2COO(o\text{-}NP)$ with the bases glycine ethyl ester, borate, morpholine, and tris(hydroxymethyl)aminomethane and of the ester $C_2H_5OOCCH(CH_3)COO(o\text{-}NP)$ with phosphate, borate, Tris, glycine ethyl ester, N-ethylmorpholine, morpholine, ethylenediamine, and triethanolamine also involve the formation of kinetically important metastable intermediates. For these cases, plots of [nucleophile] *vs.* k_{obsd} at constant pH values increase linearly with [nucleophile] at low concentrations but become independent or linearly but markedly less dependent upon [nucleophile] at higher concentrations (see, for example, the insert in Figure 1). Saturation phenomena such as these indicate a change in the rate-determining step from formation to decomposition of an intermediate and have been employed to establish the E1cB mechanism.[9] Again, as in the case of lyate species, this unusual kinetic behavior is not shown by the α,α-dimethylmalonate ester, which does not possess enolizable hydrogens. Again, as in the case

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[6] B. Holmquist and T. C. Bruice, *J. Amer. Chem. Soc.*, **89**, 4028 (1967).

[7] Any explanation based on a tetrahedral addition intermediate may be discounted: (a) on the basis that the mere formation of such an intermediate could not increase the rate of alkaline hydrolysis; and (b) the rate-determining step in the alkaline hydrolysis of *o*- and *p*-nitrophenyl esters is nucleophilic attack, so that the formation of a tetrahedral intermediate (if any) can lead only to 100% partitioning to product [see, for data and pertinent evidence, M. J. Gregory and T. C. Bruice, *ibid.*, **89**, 2121 (1967)].

[8] Where B = HO^- and H_2O, BH = H_2O and H_3O^+, E = ester, C = carbanion.

[9] D. J. McLennan, *Quart. Rev.* (London), **21**, 490 (1967).

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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[10] This work to be submitted by B. H. in partial fulfillment for the Ph.D. in Chemistry. Predoctoral fellow, National Institutes of Health, 1965–1968.

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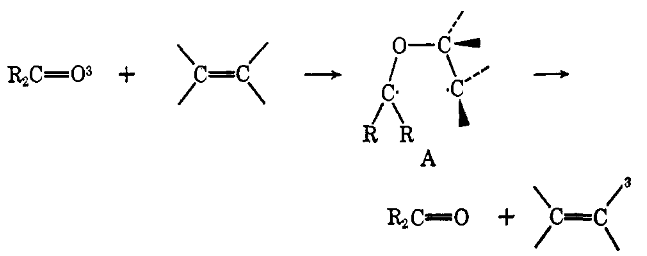
Secondary Deuterium Isotope Effects on the Transfer of Triplet Electronic Excitation to an Olefin

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 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*

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

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

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[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).

[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).