The photochemical rearrangements of **1** are subject to at least three interpretations: (i) initial formation of an *excited* diradical (**4**), which then serves as a common intermediate forming **3** by further bond cleavage and **2** by the appropriate radical recombination; (ii) formation of **2** *via* **4** as described above, accompanied by

4 5

an independent process involving a retro (2 + 2) π reaction giving *cis,trans,cis,trans*-cyclooctatetraene[13] (**5**), which is converted to *all-cis*-cyclooctatetraene under the reaction conditions (even at −60°, attempts to detect the intermediate formation of **5** were unrewarded, although experiments at much lower temperatures might yield different results); (iii) formation of **2** from **1** *via* a concerted suprafacial [1,3] sigmatropic shift, and formation of **3** by one of the above-described paths. In any event, since the thermal rearrangement of **1** to **2** (unaccompanied by **3**) seems to proceed *via* the corresponding diradical intermediate, the photochemical production of **3** from **1** must involve either a different state of this diradical or else some alternative mechanism.

(13) Known compounds similar to **5** include *trans,trans*-1,5-cyclooctadiene[14] and a *trans,cis,cis,cis*-cyclooctatetraene derivative.[15]

(14) G. M. Whitesides, G. L. Goe, and A. C. Cope, *J. Amer. Chem. Soc.*, 91, 2608 (1969).

(15) E. H. White, E. W. Friend, Jr., R. L. Stern, and H. Maskill, *ibid.*, 91, 523 (1969).

Jerrold Meinwald, Haruki Tsuruta
Department of Chemistry, Cornell University
Ithaca, New York 14850
Received February 16, 1970

Variation of Carbon-14 Isotope Effect with Substituent and the Mechanism of the *m*-Chloroperbenzoic Acid Oxidation of Labeled *para*-Substituted Acetophenones[1]

Sir:

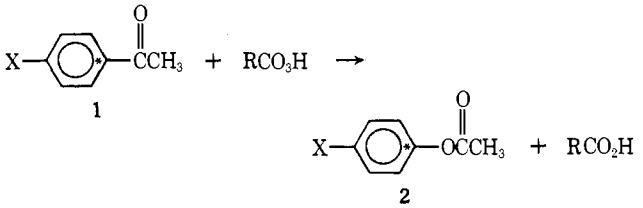
Small variations in heavy atom (nonhydrogen) isotope effects with ring substituents have been reported[2] in the past, but in no case has changing ring substitution resulted in an isotope effect change from near the lower detectable limit to near the maximum expected. Except for the recent work of Yukawa, *et al.*,[3] which was interpreted in terms of a changing mechanism with changing substituent, all previous studies of substituent effects on isotope effects have been carried out in systems in which the isotopic fractionation was taking place at an atom external to the ring bearing the substituent.

We wish to present here the results (see Table I) of a series of kinetic and isotope effect measurements on the *m*-chloroperbenzoic acid oxidation of *para*-substituted acetophenones-1-^{14}C (**1**) to *para*-substituted phenyl-1-^{14}C acetates (**2**) and to point out the implications of these results for the mechanism of the reaction.

Table I. Rates and Carbon-14 Kinetic Isotope Effects for the Oxidation of *para*-Substituted Acetophenones-1-^{14}C with *m*-Chloroperbenzoic Acid in Chloroform at 32°

para substituent	$k \times 10^3$,[a] l. mol^{-1} sec^{-1}	k^{12}/k^{14} ester[b]	k^{12}/k^{14} ketone[b]
CH_3O	40.3	0.998	0.998
CH_3	19.1	1.032	1.033
H	4.53	1.048	1.048
Cl	3.39	1.049	1.052
CN	0.50	1.084	1.085

[a] Reproducible to about 5%. [b] Calculated from the activity values of the starting ketone and the product ester or recovered ketone, respectively, at various fractions of reaction; average deviation of values from various fractions of reaction ±0.002–0.003 except for *p*-CN, ±0.006.



1 2

The labeled acetophenones were prepared from commercially available (ring labeled) benzoic-1-^{14}C acid and *p*-nitrobenzoic-1-^{14}C acid by standard methods[4–8] or as described elsewhere.[9] The kinetic and isotope effect measurements were carried out in chloroform at 32 ± 0.1°. The fraction of reaction was determined by standard iodometric methods and checked, with substantially identical results, by gas chromatographic or nmr analyses of the ketone/ester ratios. No trace of the methyl benzoate esters could be found, despite a careful search by gas chromatography. *p*-Nitroacetophenone could not be oxidized to the corresponding ester under these conditions.

All of the compounds studied displayed good second-order kinetics, in contrast to the observation of Friess and Soloway[10] that the related perbenzoic acid oxidation of substituted acetophenones displayed various kinetic orders depending on the substituent. It is clear the reaction is accelerated by electron-donating groups and slowed by electron-withdrawing groups, in general agreement with the results of Hawthorne and Emmons[11] on the related trifluoroperacetic acid oxidation of *para*-substituted acetophenones. In Hammett plots of the kinetic data, the linear fit is better with σ^+ ($\rho = -1.36$) than with σ, suggesting an activated complex which is electron deficient at a position capable of interaction with the *para* substituent. There is no indication of curvature in the Hammett plot, which supports the thesis that all of the compounds are reacting by the same mechanism.

(1) Supported by U. S. Atomic Energy Commission Contract AT-(40-1)-3234; from the Ph.D. Dissertation of B. W. P., University of Arkansas, Fayetteville, Ark., 1970.

(2) J. W. Hill and A. Fry, *J. Amer. Chem. Soc.*, **84**, 2763 (1962); J. Bron and J. B. Stothers, *Can. J. Chem.*, **46**, 1435 (1968); **47**, 2506 (1969); A. N. Bourns and P. J. Smith, *Proc. Chem. Soc. London*, 366 (1964); G. A. Ropp and V. F. Raaen, *J. Chem. Phys.*, **20**, 1823 (1952); **22**, 1223 (1954); C. G. Mitton and R. L. Schowen, *Tetrahedron Lett.*, 5803 (1968); C. G. Swain and E. R. Thornton, *J. Org. Chem.*, **26**, 4808 (1961); L. L. Brown and J. S. Drury, *J. Chem. Phys.*, **43**, 1688 (1965).

(3) Y. Yukawa, T. Ando, K. Token, M. Kawada, and S. G. Kim, *Tetrahedron Lett.*, 2367 (1969).

(4) R. E. Bowman, *J. Chem. Soc.*, 322 (1950).

(5) A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green, New York, N. Y., 1948, pp 576, 585, 647.

(6) M. Sulzbacher, E. Bergman, and E. R. Pariser, *J. Amer. Chem. Soc.*, 70, 2827 (1948).

(7) L. I. Smith in "Organic Synthesis," Coll. Vol. II, A. H. Blatt, Ed., Wiley, New York, N. Y., 1943, p 360.

(8) Full details are given in the Ph.D. dissertation of B. W. P.[1]

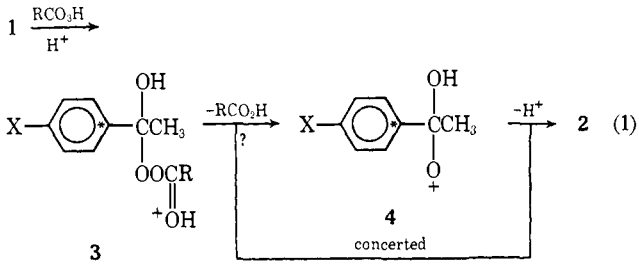
(9) B. W. Palmer and A. Fry, *J. Label. Compounds*, in press.

(10) S. L. Friess and A. H. Soloway, *J. Amer. Chem. Soc.*, 73, 3968 (1951).

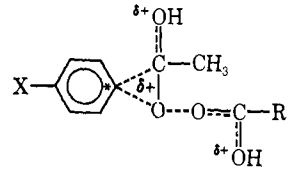
(11) M. F. Hawthorne and W. D. Emmons, *ibid.*, 80, 6398 (1958).

For each compound, isotope effect measurements were made at five fractions of reaction, ranging from 8 to 60%. The reaction mixtures were quenched with sodium hydroxide solution. For ^{14}C assay using a Beckman LS100 liquid scintillation counter,[8] the phenols resulting from basic hydrolysis of the recovered acetates were converted to benzoates and the recovered unreacted ketones were converted to oximes. The internal consistency of the isotope effect data is high, as evidenced by the relatively small errors, by the lack of any trend in k^{12}/k^{14} with fraction of reaction, and by the excellent agreement in the k^{12}/k^{14} values calculated separately from the decrease in radioactivity of product ester and the increase in radioactivity of the recovered ketone.

Most features of the mechanism of the peracid oxidation of ketones to esters are reasonably well understood.[12] For most, if not all, cases the reaction is first order in peracid and first order in ketone[11,13] and is general acid catalyzed.[11,14] The migrating group does so with retention of configuration,[15] and electron-donating substituents in the migrating group speed the reaction.[10,12] The ketone oxygen becomes the carbonyl oxygen of the ester.[16] Our version of the Criegee mechanism[17] may be applied to the present case as shown in eq 1.



The main question of timing is whether electron-deficient species **4** actually exists or whether **3** is converted to **2** (or its conjugate acid) by a concerted process. Although no previous research is definitive, most previous studies, especially that of Hawthorne and Emmons,[11] support a concerted reaction mechanism. The present isotope effect results lead unambiguously to the conclusion that the present reaction is concerted. No isotope effect would be expected for rate-determining formation of **3** or **4** since those steps do not involve significant alteration of the bonding at the labeled position.[18] Since a large isotope effect is found, neither formation of **3** nor its decomposition to **4** can be rate determining. On the other hand, in the rate-determining concerted conversion of **3** to **2**, bonding at the labeled position is extensively altered, and an isotope effect would be expected,[18] as is observed. (Of course the possibility exists that a different step might be rate determining for other compounds or conditions.) The activated complex (**5**) for this concerted reaction may be formulated as being similar to that suggested by Hawthorne and Emmons.[11]



5

The variation of isotope effect with substituent, which is far larger than the variations observed in any previous work, can be rationalized in terms of activated complex **5**. Increased bonding at a labeled position in an activated complex relative to reactants results in a decreased isotope effect; decreased bonding has the opposite effect.[18] In considering the bonding of the labeled ring carbon with the carbon at the migration origin and the oxygen at the migration terminus as the ring moves from one to the other, it is clear that different substituents will be able to satisfy the electron deficiency in the three-membered ring more or less readily. A good electron-donating group like methoxy will result in a high electron density in the three-membered ring, resulting in a "tight" activated complex with increased bonding between the ring carbon and the migration origin and terminus. This is equivalent to saying that the activated complex force constants at the labeled position are increased, and this results in a lowered isotope effect. An electron-withdrawing group will have the opposite effect, leading to a "loose" activated complex and a high isotope effect. This is exactly the trend observed experimentally. Because of the relative positions of the substituent, the labeled atom, and the electron-deficient center, a system such as the present one offers maximum opportunity for substituents to influence the isotope effect.

(12) Previous literature is very well reviewed by M. F. Hawthorne, W. D. Emmons, and K. S. McCallum, *J. Amer. Chem. Soc.*, 80, 6393 (1958).
(13) Y. Yukawa and T. Yokoyama, *J. Chem. Soc. Jap.*, 73, 371 (1952).
(14) W. E. Doering and L. Spears, *J. Amer. Chem. Soc.*, 72, 5515 (1950).
(15) K. Mislow and J. Brenner, *ibid.*, 75, 2319 (1953).
(16) W. E. Doering and E. Dorfman, *ibid.*, 75, 5595 (1953).
(17) R. Criegee, *Justus Liebigs Ann. Chem.*, 560, 127 (1948).
(18) For a qualitative review of the general concepts leading to this conclusion, and for leading references to the basic theory, see A. Fry, *Pure Appl. Chem.*, 8, 409 (1964).

(19) (a) National Science Foundation Trainee, 1965–1969; (b) to whom correspondence should be addressed.

Billy W. Palmer,[19a] Arthur Fry[19b]
Department of Chemistry, University of Arkansas
Fayetteville, Arkansas 72701
Received January 12, 1970

Structure and Stereochemical Behavior of Asymmetric α-Sulfonyl Carbanions

Sir:

Two monobromo diastereomers, mp 76° and 112°, have been obtained by bromination of either *dl*- or *meso*-bis-α-methylbenzyl sulfone with N-bromosuccinimide. Single-crystal X-ray analysis using counter data has shown that the higher melting isomer has the *erythro* configuration **1**, crystallizing in space group $P2_1/c$. All of the atoms were successfully located on a three-dimensional Fourier map phased by the bromine atom, and $R = 0.06$ for 1500 reflections above background.

Reduction of **1** with sodium sulfite or triphenylphosphine in methanol occurred in a highly stereoselective manner (90% or more) to give bis-α-methylbenzyl sulfone, mp 140°, which has been shown to be the *meso* isomer (**3**).[1] Similarly, *threo*-α-bromo-α-methylbenzyl

(1) C. Y. Meyers and A. M. Malte, *J. Amer. Chem. Soc.*, 91, 2123 (1969).