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Acetyl Peroxide Heavy Atom Kinetic Isotope Effects. A Reevaluation

Sir:

Although the "exact analysis"¹ of heavy atom kinetic isotope effects promises to provide a new and potentially powerful tool for the elucidation of transition state structure,² its scope and limitations remain still obscure. Only recently begun,³ the task of extensive testing and application has naturally tended to rely upon older methods of gas purification, mass spectrometry, and data analysis to generate the experimental kinetic isotope effects needed.

We were therefore troubled to find that the very first report^{3a,4} of such an exact analysis has since been criticized on experimental rather than on theoretical grounds.⁵ Spurious results, it was claimed, are often encountered in the traditional method of determining such isotope effects: the comparison of isotope ratios obtained from initially formed product (R_f) with those of complete reaction (R_i , eq 1).^{6,7} The

$$k_i/k_h = \ln \left[1 - f \left(\frac{1 + R_i}{1 + R_f} \right) \left(\frac{1 - R_f}{1 - R_i} \right) \right] / \ln \left[1 - f \left(\frac{R_f}{R_i} \right) \left(\frac{1 + R_i}{1 + R_f} \right) \right] \quad (1)$$

obvious culprit, contamination of the initially formed product samples, was still more strongly implicated by the subsequent independent claim⁸ that our published carbon dioxide purification techniques^{3b} were inadequate for their intended use. To eliminate such errors, the analysis of successive product fractions was instead recommended. This did indeed provide a carbon isotope effect of "less than 1.016"⁵ in contrast with our previously published 1.023 ± 0.003 .^{3a}

Concerned by the consequences of such criticism, we have now repeated the original determinations, extended the initial product range from 6 to 17%, chosen a second reaction solvent (from which the acetyl peroxide was also subjected to its final recrystallization), and used some of the "10%" carbonyl

(1) M. Wolfsberg, *Ann. Rev. Phys. Chem.*, **20**, 449 (1969); M. Wolfsberg and M. J. Stern, *Pure Appl. Chem.*, **8**, 225, 325 (1964); *J. Chem. Phys.*, **45**, 2618, 4105 (1966).

(2) M. J. Goldstein, *Science*, **154**, 1616 (1966).

(3) (a) M. J. Goldstein, *Tetrahedron Lett.*, 1601 (1964); (b) M. J. Goldstein and G. L. Thayer, Jr., *J. Amer. Chem. Soc.*, **87**, 1933 (1965); (c) S. Seltzer and S. M. Mylonakis, *ibid.*, **89**, 6584 (1967); (d) S. Seltzer, A. Tsolis, and D. B. Denney, *ibid.*, **91**, 4236 (1969); (e) A. M. Katz and W. H. Saunders, Jr., *ibid.*, **91**, 4469 (1969).

(4) An earlier application to deuterium isotope effects was reported by A. V. Willi, *Helv. Chim. Acta*, **47**, 647, 655, 837 (1964).

(5) J. W. Taylor and J. C. Martin, *J. Amer. Chem. Soc.*, **89**, 6904 (1967).

(6) This differs from eq V.21 of ref 7 only by its inclusion of the numerically insignificant $(1 - R_f)/(1 - R_i)$ term that arises whenever 2 mol of analyzed product (CO_2) is formed. Cf. J. Warkentin and D. M. Singleton, *Can. J. Chem.*, **45**, 3045 (1967).

(7) J. Bigeleisen and M. Wolfsberg, *Advan. Chem. Phys.*, **1**, 15 (1958).

(8) T. Koenig and R. Cruthoff, *J. Amer. Chem. Soc.*, **91**, 2562 (1969).

¹⁸O-enriched substrate originally prepared for another purpose.⁹ These, we would think, should provide ample opportunity to observe the consequences of otherwise hidden impurities. The results shown in Table I

Table I. Carboxyl Kinetic Isotope Effects^a

Solvent	Temp, °C	f_{max}^b	n^c	k_{12}/k_{13}	k_{16}/k_{18}
Cumene	44.7	0.05	9	1.019 ± 0.001	1.035 ± 0.002
	44.7	0.15	5	1.016 ^d ± 0.007	1.0337 ^d ± 0.0007
Isooctane	44.8	0.06	5	1.023 ^e ± 0.003	1.023 ^e ± 0.007
	44.4	0.13	3	1.0212 ± 0.0001	1.027 ± 0.001
	44.7	0.17	6	1.023 ^d ± 0.002	1.029 ^d ± 0.002
	80			<1.016 ⁱ	1.033 ⁱ
	74	0.07	6		1.021 ^{e,h}
	74	0.07	6		1.020 ^{f,h}

^a Uncertainties are standard deviations; isotopic abundances are at natural levels except where noted otherwise; italicized entries are from other laboratories. ^b Maximum extent of partial decomposition. ^c Number of independent partially decomposed samples analyzed. ^d 10% carbonyl ¹⁸O-enriched. ^e Hexadeuterated. ^f 1.4% carbonyl ¹⁸O-enriched. ^g Reference 3a. ^h Reference 8. ⁱ Reference 5.

leave little question as to the reproducibility and reliability (if not also the accuracy) of the originally published data. Of particular note is the insensitivity of our oxygen isotope effects to a 50-fold variation in ¹⁸O distribution between carbonyl and peroxidic oxygens, a necessary consequence of oxygen scrambling.^{9,10}

We chose not to employ the recommended⁵ method of successive product fractions¹¹ because: (a) the expected⁵ linear plot of "ln A" vs. ln(1 - f) should in fact obtain only in the limit of infinitely small product fractions, an experimentally inconvenient restriction. (b) Finite fractions require the use of equations, properly judged to be "awkward... for systematic treatment of the experimental data."⁷ (c) All such equations presume an infinitely small isotope ratio. Well-justified in the ¹⁴C studies for which they were originally intended,¹¹ their application to our own heavy isotope abundances of 0.4–10% seemed questionable.¹²

Curiously, the same authors⁴ also reported determination of a methyl carbon isotope effect, $k_{12}/k_{13} = "1.005-1.010,"$ that appeared to provide unanticipated support for our original mechanistic conclusion.^{3a} Repeating their approach (CuO oxidation of the methane product), but using traditional methods of purification and analysis, we now find their published data to be consistent only in their unreliability. In two solvents, the carbon isotope effect at the methyl is less than

(9) M. J. Goldstein and H. A. Judson, *ibid.*, **92**, 4119 (1970).

(10) More rigorously, such insensitivity should always follow so long as the difference between rates of scrambling and decomposition exceeds the difference between the decomposition rates of isotopically differing reactants. For the dependence of apparent isotope effect on isotopic distribution in the absence of scrambling, see eq A2 in ref 3b.

(11) A. M. Downes, *Aust. J. Chem. Res.*, **5**, 521 (1952).

(12) The results of ref 5 derive from 5% ¹³C-enriched substrate. No details of fraction size were provided.

Table II. Methyl Carbon Kinetic Isotope Effects^a

Solvent	Temp, °C	f_{max}^b	n^c	k_{12}/k_{13}
Cumene	44.7	0.02	4	1.0038 ±0.0005
Isooctane	44.4	0.13	3	1.0029 ±0.0007
	80			<i>"1.005-1.010"</i> ^d

^a Uncertainties are standard deviations; italicized entries are from other laboratories. ^b Maximum extent of partial decomposition. ^c Number of independent partially decomposed samples analyzed. ^d Reference 5.

that at the carboxyl carbon by almost an order of magnitude¹³ (Table II).

Finally, we would hope that the reproducibility noted in Table I might carry with it the implication that similarly obtained results from our own and other laboratories be (at least initially) regarded as no less reliable.

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(13) As empirical orientation, the acetylenic and nitrile k_{12}/k_{13} measured for dicyanoacetylene addition to cyclopentadiene at 0° are 1.0204 and 1.0003 (C. B. Warren, Ph.D. Thesis, Cornell University, Ithaca, N. Y., 1970).

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Reaction of Excited Triphenylcarbonium Ion with Oxygen^{1a}

Sir:

In the relatively unexplored area of carbocation photolysis,^{1b} the triphenylcarbonium ion case possesses special significance because of the widespread interest in the photochemistry of structurally related dyes, especially those used as sensitizers for singlet oxygen reactions. We describe herein the irradiation-induced behavior of the parent trityl case with oxygen.

When triphenylcarbonium ion in 3.3% H₂SO₄-96.5% CH₃CO₂H-0.2% H₂O was photolyzed under oxygen with visible light,² there were formed benzo-

(1) (a) Part II of a series concerned with the photolysis of triphenylcarbonium ion; (b) the first studies involving identification of photoproducts derived from carbonium ion cases were reported by E. E. van Tamelen, T. M. Cole, R. Greeley, and H. Schumacher, *J. Amer. Chem. Soc.*, **90**, 1372 (1968).

(2) All photolyses were carried out using a 450-W Hanovia medium-pressure lamp surrounded by a uranium(VI) glass filter. The carbonium ion source was triphenylcarbinol (*ca.* 10⁻³ M). Control experiments indicated that covalent trityl compounds are not photolyzed under these conditions. Furthermore, energy transfer from triplet triphenylcarbonium ion to covalent trityl compounds would be highly endothermic. On the basis of its phosphorescence spectra trityl cation has $E_T \sim 50$ kcal/mol.³ On the basis of published phosphorescence data, covalent trityl species have $E_T \sim 70$ kcal/mol.⁴

(3) In 96% sulfuric acid at room temperature triphenylcarbonium ion exhibits weak fluorescence ($\phi_F \sim 0.01-0.001$) with maxima at *ca.* 520 and 540 nm. At -196° in a sulfuric acid glass trityl cation has a phosphorescence maximum at 545 nm ($\phi_P/\phi_F \sim 20$) (we thank Professor L. Stryer for the fluorescence and phosphorescence measurements). From its ϵ of 4×10^4 at λ_{max} 410, 430 nm and the absence of fluorescence under nitrogen ($\phi_F < 0.001$) in the 3.3% sulfuric acid-acetic acid system, the singlet lifetime of the trityl cation can be roughly estimated to be $< 2.5 \times 10^{-12}$ sec in this system (J. G. Calvert and J. N. Pitts, Jr.,

phenone (37%), diphenylmethylenedioxybenzene (I; 30%),⁵ and a substance, C₂₁H₁₈O₄,⁶ mp 116-118° (11%), assigned structure II. In addition to the molecular ion at 334, the mass spectrum of II displayed a first fragmentation peak at 302 (-O₂), then *inter alia* 274 (-CH₃COOH) and 243 (base peak, -O₂ and CH₃CO₂).⁶ The uv spectrum revealed maximal absorption at 260 nm (ϵ 3600), while carbonyl absorption in the ir fell at 5.72 μ . Proton resonances (CDCl₃ solvent, 60 MHz) appeared at τ 7.92 (3 H, singlet, acetate), 4.85-3.90 (5 H, complex multiplet), and 2.67 (10 H, aromatic singlet). Catalytic reduction (5% Rh-C in aqueous methanol) led to a triol monoacetate (III) which was inert to sodium metaperiodate. In the infrared, the reduction product displayed peak absorption at 2.92 (-OH) and 5.81 (acetate) μ . An nmr spectrum (CDCl₃, HA 100) included the following signals: τ 8.00 (3 H, singlet, acetate), 8.6-7.8 (4 H, multiplet, methylene), 6.65 (1 H, broad singlet, hydroxyl), 5.78 (1 H, multiplet, >CHO), 5.47 (1 H, broad singlet, hydroxyl), 5.06 (1 H, multiplet, olefinic), 4.68 (1 H, multiplet, olefinic), and 2.76 (10 H, singlet aromatic). After D₂O exchange, the τ 5.47 and 6.65 signals disappeared while the τ 5.78 peak sharpened into a doublet.

At lower acid concentrations (1% H₂SO₄) triphenylcarbonium ion provided on photolysis an aldehyde acetate (IV) in addition to the above products. This substance possessed (high-resolution mass spectrum) the formula C₂₁H₁₈O₄.⁶ In addition to the molecular ion, the low-resolution mass spectrum included fragmentation peaks at *m/e* 292 (-CH₂CO), 274 (base peak, -CH₃CO₂H), and 245 (-CH₃CO₂H and CHO). Carbonyl absorption appeared in the ir at 5.71 and 5.88 μ and in the uv at 298 and 309 nm (conjugated). In an nmr analysis, the aldehyde displayed signals at τ 8.25 (3 H, singlet), 4.20-3.70 (4 H, complex multiplet), 2.81 (10 H, singlet), and 0.75 (1 H, singlet). Saponification provided the expected aldehyde alcohol, whereas reduction with sodium borohydride effected simple conversion of the aldehyde function to the corresponding alcohol (λ_{max} 264, 270 nm).

Because under conditions of complete light absorption the rate of disappearance of triphenylcarbonium ion was independent of its concentration, a mechanism involving the formation of singlet oxygen and its subsequent reaction with ground-state carbonium ion (or trityl acetate) seems unlikely.⁷ Furthermore, the ready reaction of singlet oxygen with triphenylcarbonium ion would not be expected, as singlet oxygen is thought to be electrophilic.⁷ A simple mechanism consistent with the above observations is shown in Scheme I.

It seems most reasonable to assume that it is the excited triplet state of the carbonium ion that is under-

"Photochemistry," Wiley, New York, N. Y., 1966, p 174; N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1967, p 54), which would seem to be too short to allow appreciable reaction with oxygen at *ca.* 10⁻² M (E. W. Washburn, Ed., "International Critical Tables of Numerical Data, Physics, Chemistry and Technology," Vol. III, McGraw-Hill, New York, N. Y., 1928, p 263).

(4) Yu. I. Kozlov and D. N. Shigorin, *Dokl. Akad. Nauk SSSR*, **161**, 871 (1965); *Chem. Abstr.*, **63**, 6528 (1965).

(5) The 1,2-diphenylmethylenedioxybenzene was identified by spectral and mixture melting point comparison with authentic material.

(6) The high-resolution mass spectrum was obtained on a MS-9 direct inlet machine. The low-resolution mass spectrum was obtained on an Atlas direct inlet machine.

(7) C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968).